PB-242 293

# LITERATURE STUDY OF SELECTED POTENTIAL ENVIRONMENTAL CONTAMINANTS TITANIUM DIOXIDE

ARTHUR D. LITTLE, INCORPORATED

PREPARED FOR

ENVIRONMENTAL PROTECTION AGENCY

MAY 1975

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| | | |
|---|---|---|
| 1. REPORT NO.<br>EPA-560/2-75-001 | 2. | 3. PB 242 293 |
| 4. TITLE AND SUBTITLE<br>Literature Study of Selected Potential Environmental Contaminants<br>Titanium Dioxide | | 5. REPORT DATE<br>May 1975 |
| | | 6. PERFORMING ORGANIZATION CODE |
| 7. AUTHOR(S) | | 8. PERFORMING ORGANIZATION REPORT NO.<br>C-77354 |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS<br>Arthur D. Little, Inc.<br>Acorn Park<br>Cambridge, Massachusetts 02140 | | 10. PROGRAM ELEMENT NO.<br>2LA328 |
| | | 11. CONTRACT/GRANT NO.<br>68-01-2688 |
| 12. SPONSORING AGENCY NAME AND ADDRESS<br>Office of Toxic Substances<br>Environmental Protection Agency<br>Washington, D.C. 20460 | | 13. TYPE OF REPORT AND PERIOD COVERED<br>Final |
| | | 14. SPONSORING AGENCY CODE |

15. SUPPLEMENTARY NOTES

16. ABSTRACT

A comprehensive review of the literature published since 1 January 1954 was conducted to prepare this preliminary report on the physical and chemical properties of titanium dioxide ($TiO_2$), on the environmental exposure factors related to its consumption and use, on the health and environmental effects resulting from exposure to $TiO_2$, and on the regulations and standards governing its use.

Titanium dioxide is industrially significant because of its unique contribution to the manufacture of such commonly-used products as paint, paper and plastics. Historically, $TiO_2$ has been recognized as an innocuous compound, but it is classified as a nuisance dust to which prolonged exposure can cause respiratory irritations. Current problems include concern about the future availability of rutile ore to supply the increasing number of facilities using this ore in the chloride manufacturing process, and the disposal of the high volume of $TiO_2$ manufacturing wastes, particularly the spent sulfuric acid and ferrous sulfate from the sulfate manufacturing process. On the basis of reported information, $TiO_2$ does not pose substantial environmental hazard.

17. KEY WORDS AND DOCUMENT ANALYSIS

| a. DESCRIPTORS | | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group |
|---|---|---|---|
| anatase | pollution | environmental exposure | 06/F,J,T |
| environmental contaminants | utilization | environmental effects | 07/B,D |
| pigments | | physical properties | |
| rutile | | chemical properties | |
| titania | | | |
| titanium dioxide | | PRICES SUBJECT TO | CHANGE |
| production capacity | | | |

| | | |
|---|---|---|
| 18. DISTRIBUTION STATEMENT<br>Release unlimited | 19. SECURITY CLASS *(This Report)*<br>unclassified | 21. NO. OF PAGES<br>131 |
| | 20. SECURITY CLASS *(This page)*<br>unclassified | 22. PRICE<br>5.75 |

Form 2220-1

EPA-560/2-75-001 168189

PB242293

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# TITANIUM DIOXIDE

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## FINAL REPORT

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EPA-560/2-75-001

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# OF
# SELECTED POTENTIAL
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## TITANIUM DIOXIDE

FINAL REPORT

May 1975

Contract No. 68-01-2688

Office of Toxic Substances
Environmental Protection Agency
Washington, D.C. 20460

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Project Officer

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C-77354

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# SUMMARY

## 0. INTRODUCTION

Titanium dioxide ($TiO_2$) is the most important oxide of titanium, deriving this importance primarily from its extensive use as a white pigment in a variety of commercial products. Principal raw materials for the manufacture of $TiO_2$ by two major processes -- the sulfate process and the chloride process -- are the minerals ilmenite and rutile.

Ilmenite, an iron-black mineral composed of iron, titanium, and oxygen, occurs in plentiful supply throughout the world and is mined extensively in many countries, including the United States. In 1967, world production of ilmenite rose to approximately 3 million short tons per year and since then has remained at that level or increased slightly. Of this amount, the U.S. produces about 700,000 short tons. Ilmenite (40-60% $TiO_2$) has been the source of the titanium dioxide produced by the sulfate process, but recently Du Pont started to use that ore in its chloride process.

Rutile, which is a reddish-brown mineral of almost pure titanium dioxide (usually containing a little iron), occurs chiefly in Australia. No rutile is mined in the United States, but current world production is approximately 400,000 long tons per year. At this rate, world supplies are expected to last only 20-25 years, a situation with serious overtones since rutile is the basic raw material for most chloride production of titanium dioxide.

One potential source to offset the question of rutile reserves is the upgrading of ilmenite to over 90% $TiO_2$ through the removal of iron. It can then be processed, utilizing the rutile chloride technology. This removal of part or almost all of the iron content of the ilmenite ore results in a product soluble in sulfuric acid, or one which can be chlorinated economically, and is the nature of the beneficiation process. The relative abundance of ilmenite compared to rutile makes beneficiation of ilmenite a promising technology. Some ilmenite producers and rutile consumers alike are converting to the beneficiation route. In addition, one manufacturer has developed a process to use mixed ores in the feed; other manufacturers are developing technology so that unbeneficiated ilmenite can be chlorinated.

With U.S. production capacity for titanium dioxide predicted at 939,000 tons per year, its potential impact on the environment was deemed worthy of study. This report reflects the findings of a comprehensive review of the literature published during the last 20 years on the physical and chemical properties of $TiO_2$, on the environmental exposure factors related to its consumption and use, on the health and environmental effects resulting from exposure to $TiO_2$, and the regulations and standards governing its use. In summary, the literature provides the following information.

## I. PHYSICAL AND CHEMICAL DATA

Titanium dioxide, a white crystalline material that occurs naturally in many minerals, is an inert compound, very resistant to chemical attack by most acids and alkalies. It has a high refractive index, a property that enables it to refract or bend light rays and thus to impart whiteness and opacity to paints and other products in which it is used.

Its insulating properties have made it attractive to the plastics and ceramics industries, and its dielectric and semiconducting properties contribute to its usefulness in electronic components.

Titanium dioxide, whether manufactured from ilmenite or rutile ore, can be produced in two crystalline forms -- anatase or rutile. These manufactured crystals have properties very similar to the natural crystals, crystals that exist in the ores of the same names.

The manufactured pigments, or powders, are white, but the rutile-type is generally a yellowish-white, while the anatase is more apt to have a bluish cast. The pigments are odorless, inert, and melt at over 1800°C.

Although every effort is made to produce a "pure" $TiO_2$, the end product usually contains a small percentage of one or more of the oxides of aluminum, silicon, zinc or antimony, compounds that are used in the manufacturing process to impart particular properties to the pigment. In some instances, a very small amount (in the range of parts per million) of metals, e.g., iron, chromium, vanadium, are present.

Titanium dioxide is treated with metal oxides during the manufacturing process to reduce its photoreactivity. Untreated pigments, apparently, can contribute to the photodegradation of organic systems exposed to ultraviolet radiation.

## II. ENVIRONMENTAL EXPOSURE FACTORS

### A. Production and Consumption

Titanium dioxide was first produced in the U.S. in 1916 by the Titanium Pigment Company. In 1925 (after the National Lead Company had purchased a large interest in the Titanium Pigment Company), production reached 4,000 tons. By 1971, there were eight United States producers with a combined estimated capacity of about 800,000 tons. In 1974, nine U.S. manufacturers had a production capacity of 939,000 tons of $TiO_2$.

Production in 1972 was approximately 700,000 tons, while apparent consumption was about 787,000 tons, including imports. Imports have ranged from 5% to 10% of total apparent consumption in recent years and are expected to remain at about this percentage level. Exports, less than 2% to 3% (about 15,000 tons) of production from 1966 through 1971, declined in 1972.

The paint, paper and plastics industries accounted for almost 80% of the 787,000 tons consumed in 1972, a tonnage valued at about $433 million on a delivered basis.

In the U.S., the current plant capacity for producing titanium dioxide is divided almost equally between the two major production processes -- the sulfate process and the chloride process. In recent years, new U.S. plants have been built to accommodate the latter process because of such factors as lower investment and production costs, better product quality, and reduced quantities of waste.

U.S. titanium dioxide producers are located in Ohio, New Jersey, Delaware, Maryland, Tennessee, Mississippi, Missouri, Georgia, and California.

Chemically pure $TiO_2$ is prepared from rutile ore, which is chlorinated and yields titanium chloride (principally titanium tetrachloride) vapors. These vapors are then oxidized to $TiO_2$ in a burner supplied with air, the burning or oxidation operation being the chief factor in a successful process. A number of intermediate steps, of course, are necessary in this process to remove impurities. Later, after the finely-divided $TiO_2$ is produced, various metallic or non-metallic oxides are added to control pigment properties; additional treatment provides optimum pigment properties. Ilmenite ore can be substituted for rutile in this chloride process, but more chlorine is required, making the process costs higher.

Ilmenite is generally used to make $TiO_2$ by the sulfate process. In this method, ground ilmenite plus sulfuric acid, iron and water are mixed in a digester (using air agitation), and then the soluble titanium and iron sulfates are leached from the reaction mass. Other steps involve the separation of the titanium from contaminating iron salts, and the conversion of the titanium sulfate to titanium hydrate, which is then calcined (heated to a high temperature) to form crystalline titanium dioxide. The crystalline material (generally the anatase form) is then milled, treated to obtain certain properties, and packaged for sale.

In the early and mid-1950's, there was a dramatic increase in the market price of titanium dioxide, but over the last 20 years the price of anatase pigment increased only by about 6.5¢/lb and that of rutile about 7¢/lb. From 1965 to 1971, prices were fairly stable for both forms, anatase selling for 25¢/lb in 1961 (car lot price) and for 26¢ in 1971; rutile selling for 26¢ in 1965 through 1968, for 27¢ in 1969 and 1970, and for 26¢ again in 1971.

In more recent years, however, rising costs of production and pollution control have caused price increases. In late 1974, NL Industries announced additional increases for various grades of $TiO_2$. For less than five tons, this company's rutile grades now cost 43 to 44¢/lb, while the anatase pigments sell for 35 to 43¢/lb.

There has been a steady upward growth in the production of titanium dioxide and this growth is expected to increase into 1975. Nevertheless, there are signs of a slowing in production (718,000 tons in 1972, 772,000 in 1973, 815,000 in 1974, and 835,000 estimated for 1975), and some estimators believe that demand may catch up to production capacity by 1976.

Market trends are influenced by the availability of raw materials and problems of waste disposal. Although the supply of ilmenite seems assured because of known, extensive deposits, known reserves of rutile may be depleted within 25 years. To counteract the potential shortage of rutile, efforts are being made to beneficiate the ilmenite ore (i.e., to remove iron from the the ilmenite raising its $TiO_2$ content to 90+%). A more pure ilmenite can then be used economically in the chloride process. Yet, an ilmenite that will still be soluble in sulfuric acid is needed for the sulfate process. Some producers are adopting beneficiation; one is using mixed ores to produce $TiO_2$; and others are attempting to find ways of economically chlorinating unbeneficiated ilmenite.

The problems of waste and waste disposal may be considered influences on future market potentials for $TiO_2$. Air pollutants from the sulfate process require control devices, such as wet scrubbers, to remove particulates, and pollution control devices generally add to production costs. One of the waste products from the sulfate process is ferrous sulfate, or copperas, a product that has little market potential because supply seems always to exceed demand. Although new uses for copperas, e.g., in water treatment, have been sought, so far little progress has been made. Therefore, much of the copperas must be disposed of as waste, under increasingly strict waste-disposal laws.

Even though chlorine is recycled in the chloride process, gaseous pollutants do exist, and pollution control requirements will contribute to changing market prices and, possibly, to reduced market demands.

## B. Uses

Some 700,000 to 800,000 short tons per year of $TiO_2$ are consumed in the United States. In 1972, the three major users -- the paint, paper, and plastics industries -- accounted for 626,000 of the total 787,000 short tons of $TiO_2$ consumed in the U.S. The remainder was used, in decreasing amounts, by such industries as rubber, floor covering, printing ink, ceramics, synthetic fibers, and roofing granules. Miscellaneous uses accounted for 40,000 short tons.

For most of the above uses, there appears to be no alternative material that can be substituted for $TiO_2$. The one exception, however, is the paper industry, which finds that lower-priced alumina and silica clays provide brightness almost equal to that obtained with titanium dioxide.

## C. Environmental Contamination Potential (Sources)

Principal environmental contaminants derive from impurities in the ores used as raw materials in the manufacture of $TiO_2$, additives used in the processing of the material, and by-products and wastes generated in the manufacturing processes. The main problem appears to center around the high volume of wastes and their disposal.

The major wastes from the sulfate process are the spent sulfuric acid and ferrous sulfate (copperas). Because the latter is in plentiful supply and can be manufactured at low cost from certain iron scrap, there is, therefore, little market demand for the copperas waste from $TiO_2$ production and little incentive for $TiO_2$ producers to invest in equipment to recover it. Waste disposal of copperas involves certain expenses and must satisfy existing waste-disposal regulations. It does not appear to be economically feasible, either, to recover the sulfuric acid from the waste. Thus, producers of $TiO_2$ by the sulfate process must neutralize their acid wastes to meet water quality standards.

From the chloride process, some chlorine and product dusts are potential air pollutants, but the magnitude of these gaseous wastes may be considered small when compared with the control of small particulates from other industries. The non-volatile wastes, e.g., metallic impurities in the ore, carbon, and unreacted ore have, generally, been considered non-hazardous. Effluents contain titanium hydroxide and small amounts of metal compounds.

Titanium tetrachloride, the precursor of $TiO_2$ in the chloride process, is also used in the manufacture of titanium metal. Titanium tetrachloride is hazardous because it decomposes in a moist atmosphere, generating $TiO_2$ and hydrochloric acid. Chlorine is recycled. Most of the other products involved are considered wastes and proper control equipment and/or waste disposal methods must be considered for cost effectiveness and for compliance to environmental disposal laws.

There are restrictions on ocean dumping and there is a possibility that some trace metals (e.g., arsenic, chromium, copper, mercury, lead) may leach out of $TiO_2$ solid wastes used as landfill.

No unusual environmental situations seem to be associated with the packaging, transport or storage of titanium dioxide, which is generally shipped in paper sacks. In its industrial use, dust and fumes from electric furnace operations may present a problem. Inhalation of $TiO_2$ above the OSHA employee exposure limit (8-hour time weighted average: 15 $mg/m^3$) can cause irritation to workers exposed to the dust or fumes.

## D. Current Handling Practices and Control Technology

Under normal working conditions, however, there are no occupational safety and health recommendations governing eye protection, protective gloves, or respiratory protection for those handling titanium dioxide. When concentrations of $TiO_2$ exceed the 8-hour time weighted average, established by OSHA at 15 $mg/m^3$, protective gloves and glasses are required.

Under conditions of excessive dusting and/or for clean-up purposes, a non-toxic particle mask and ventilation, such as mechanical exhaust, is desirable. A dust respirator is required when an employee's exposure in any 8-hour work-shift of a 40-hour week will exceed the 8-hour time weighted average.

The fact that no major disasters have been associated with titanium dioxide, coupled with its reputation as an inert material, argues for the lack of stringent regulations in its shipment and storage. It is shipped in paper sacks, containing approximately 50 pounds, or as a slurry in water in tank trucks or rail cars. Few precautions are taken in storing $TiO_2$ other than the avoidance of damp or wet storage, which causes caking.

Methods practiced for the disposal of waste from the manufacture of $TiO_2$ include ocean dumping, landfill, and deep-well injection. Acidic wastes are neutralized before disposal. Where feasible, waste products are recycled or recovered for sale.

No widespread incidence of adverse effects on marine life has been reported from ocean dumping, although one study indicates that there may be an effect on the sand dollar. Environmental protection authorities are, however, questioning the feasibility of ocean dumping, and manufacturers have also shown some concern about the continuation of this practice.

Standard protective equipment, as described above, is required, if $TiO_2$ is spilled or leaked.

There are no restrictions on the composition of $TiO_2$ used in packaging or food contact applications but, when $TiO_2$ is used as a color additive in foods, drugs, or cosmetics, its composition must comply with the standards established by the U.S. Food and Drug Administration.

### E. Monitoring and Analysis

The variety of analytical methods used for determining the composition and character of wastes from the manufacture of $TiO_2$ are standardized procedures in general use.

## III. HEALTH AND ENVIRONMENTAL EFFECTS

### A. Environmental Effects

Titanium dioxide is inert chemically. It is insoluble in water and most acids. Since the suggested waste disposal methods for producers is sanitary landfill, $TiO_2$ is considered persistent with no evidence of chemical or biological degradation.

Titanium dioxide is accumulated to a lesser extent in plants, fish, mice, etc., than are the soluble salts of titanium, such as potassium titanium oxylate.

## B. Biology

Laboratory studies with animals on a diet containing 0.25% $TiO_2$ for 13 days demonstrated over 90% excretion of the total dose in the feces with little or no absorption from the digestive tract.

No absorption of $TiO_2$ is observed after skin application.

There is deposition of $TiO_2$ in the lungs and lymph nodes in rats subjected to inhalation and intratracheal injection experiments. Silica-containing dust shows greater absorption in the lungs than $TiO_2$ dust, during intratracheal studies.

Intravenous injection of 1 and 2 mg of $TiO_2$ in rats produced no appreciable change in blood platelet count. A dose of 4 mg, however, caused a marked decrease in platelet count. Comparatively, a similar decrease in the number of circulating blood platelets was noted after injection of only 1 mg of synthetic silica.

Titanium and its alloys have been tested as a surgical implant in animal tests with no apparent adverse effects on either tissues or bones.

## C. Toxicity -- Humans

No widespread incidence of illness among workers exposed to $TiO_2$ or titanium dust has ever been reported. According to a report from Finland, however, three men, who had worked in a $TiO_2$ processing factory for about 10 years, had lung problems including difficult or hard breathing, a cough and recurrent bronchitis associated with their work. Lung examination of two of the patients revealed changes related to lung disease due to the inhalation of fine particles (pneumoconiosis). Surgical incision of the wall of the chest (thoracotomy) showed one patient had lung membrane adhesions and green-colored patches on the lung surface associated with carbon, plus pigment aggregations due to an unidentified pigment. One lung showed emphysema and chronic bronchitis, and x-ray fluorescence analysis indicated the presence of large amounts of titanium in the lungs of all three men.

In a larger study, however, examination of 136 workers who processed ilmenite ore (titanium oxide with iron present), showed little incidence of serious adverse effects. These individuals had worked with the titanium ore for one to twelve years, with an average of 3.3 years service for the most exposed workers. Radiological lesions were found in three workers, only one of whom had a high degree of exposure. All three showed no symptoms. Six workers showed respiratory symptoms since starting work at the factory but none had abnormal physical signs or radiological lesions. The symptoms were not judged to be a specific response of the workers to the titanium minerals but were attributed to the dust per se.

A health survey, conducted by NIOSH, at one titanium dioxide manufacturing plant in New Jersey on 15 randomly-selected workers revealed no health complaints by these individuals nor knowledge of ill health of any of their associates. Nine workers with health complaints were interviewed; none of these suggested a relationship to exposure to titanium dioxide. Although the plant was rather dusty, respirable levels of $TiO_2$ were below the standards permitted.

No studies on widespread diseases related to $TiO_2$ were found in the literature. Titanium and its compounds have long been used in surgical appliances and in the treatment of skin disorders with no reports of resulting toxicity.

There is little data available on controlled studies of the toxicity to humans of titanium dioxide. Conversely, the use of titanium salts in ointments and powder preparations over a 3-year period in about 100 cases showed healing but not toxic effects. Also, $TiO_2$ is reputedly useful in protecting the skin from exposure to light; and, in cosmetics, pure $TiO_2$ paste has not shown any adverse effects.

### D. Toxicity -- Birds and Mammals

Rats receiving a single intratracheal injection of $TiO_2$, 20 mg per animal, showed no adverse reactions. No other studies pertaining to the acute toxicity of $TiO_2$ were located.

Inhalation studies over a period of 9-13 months showed no evidence of any specific pathologic lesion (body organ damage) in rats.

### E, F, G. Toxicity -- Other Organisms

No studies on the toxicity of $TiO_2$ to lower animals, plants, and/or microorganisms were found.

### H. Effects on Inanimate Objects and Structures

The literature did not reveal any information on the effects of $TiO_2$ on materials.

## IV. REGULATIONS AND STANDARDS

### A. Current Regulations

Under the Federal Food, Drug and Cosmetic Act, $TiO_2$ used as a color additive, must be free from admixture with other substances and may not contain more than very minute amounts of lead, arsenic, antimony, and mercury.

When used as a coloring in foods, amounts of $TiO_2$ used may not exceed 1% by weight of the food.

The EPA identifies $TiO_2$ as a material "requiring special care" for ocean dumping, and as a processing waste "requiring special care." OSHA has set an exposure limit level for industry, but DOT does not include $TiO_2$ on its list of hazardous materials, and it does not appear on the National Safety Council's list.

Titanium dioxide does not appear on the list of dangerous goods published by the Inter-Governmental Maritime Consultative Organization.

The American Conference of Governmental Industrial Hygienists classifies $TiO_2$ as a "nuisance dust" and, in accordance with the general rule for substances in this category, they recommend a TLV of 10 $mg/M^3$ for $TiO_2$. In its summary of hygienic standards, the American Industrial Hygiene Association concludes that it is unlikely that an emergency requiring medical attention could arise from exposure to $TiO_2$.

Finally, the Joint Group of Experts on the Scientific Aspects of Marine Pollution (GESAMP), comprised of IMCO, FAO, UNESCO, WMO, IAETA, and UN experts, classifies $TiO_2$ wastes as a slight harm to living resources, a negligible hazard to human health, and a negligible hindrance to maritime activities.

## V. EVALUATION AND COMMENTS

### A. Summary

Titanium dioxide is an industrially significant high volume chemical. In itself, it is not considered hazardous, but it is a nuisance dust, causing respiratory irritations. Such irritations, however, in no way compare to the adverse effects of silica and asbestos. Environmental concern centers about the waste products from $TiO_2$ manufacture.

## B. Conclusions

Manufacturers face the problem of a depleting supply of a major raw material for one manufacturing process, and continuing problems of processing waste disposal.

A study of the effects of the leaching of trace metals from solid $TiO_2$ waste is indicative of suggested research studies.

Lack of information on many parameters bearing on the health and environmental effects of $TiO_2$ hinder analysis and evaluation. In general, the presently available information on $TiO_2$ *per se* indicates no environmental hazard potential. However, the type and volume of wastes from $TiO_2$ production give rise to significant pollution control problems.

# PRELIMINARY INVESTIGATION REPORT

## I. PHYSICAL AND CHEMICAL DATA

Titanium forms four well-defined oxides of which the dioxide is the only one of real importance and commercial interest.

### A. Structure and Properties

### 1. Chemical Structure

Titanium dioxide is identified as:

| | | |
|---|---|---|
| Chemical formula: | | $TiO_2$ |
| Chemical composition (wt%): | Ti | 59.96 |
| | O | 40.04 |
| | | 100.00 |
| Molecular weight: | | 79.90 |

Synonyms include:

Titania
Anatase titanium dioxide
Rutile titanium dioxide

Trade names include:

| | |
|---|---|
| Ti-Pure® R-900 | (DuPont) |
| TITANOX® 2032 | (NL Industries) |
| TRONOX CR-892 | (Kerr-McGee) |

### 2. Mixture Information

Not applicable.

## 3. Physical Properties of Pure Material

Titanium dioxide is a white crystalline material that occurs naturally in three crystal forms: anatase, rutile, and brookite. The two commercially important forms, anatase and rutile, are tetragonal crystals. Brookite, which is orthorhombic, is, however, rare and of no commercial importance. Although substantially pure $TiO_2$, these crystals are of a dark color because of the presence of small amounts of impurities, particularly iron and iron oxides and, in some instances, minute amounts of non-ferrous metallic oxides.

Rutile is thermally stable; anatase less so, transforming to rutile between 700° to 950°C. Physical properties of the natural crystals are maintained by the manufactured crystals and are described later. (See:pp. 3-4)

Both the anatase and rutile crystalline forms of $TiO_2$ resist chemical attack. Resistance to acid contributes to the use of $TiO_2$ in vitreous enamels applied on ferrous surfaces.

The outstanding ability of $TiO_2$ to refract or bend light rays and thus impart whiteness and opacity to the media in which it is used, accounts for its commercial importance. Rutile has the highest refractive index of any white pigment, 2.76, while the refractive index of anatase is 2.55. For this reason the rutile grades of ore with higher, more economical, opacity and tinting strength are generally preferred. On the other hand, the anatase grades of ore impart a bluer tone, whereas the rutile has a yellow cast.

The insulating properties of $TiO_2$ contribute to its usefulness in the plastics and ceramics industries. Some selected electrical properties for rutile titanium dioxide are given in the table following.(1)

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1. W.A. Kampfer, "Titanium Dioxide," Pigment Handbook, Volume 1. Temple C. Patton, Editor (New York: John Wiley & Sons, Inc., 1973) p. 6 Copyright © 1973 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

## TABLE I

## SELECTED ELECTRICAL PROPERTIES OF TITANIUM DIOXIDE

| | Rutile | Anatase |
|---|---|---|
| Dielectric constant | | |
| Pigment | 114 | 48 |
| Single crystal | | |
| *a*-direction | 170 | — |
| *c*-direction | 86 | |
| Loss tangent | | |
| *a*-direction | 0.0110 to 0.0002 | — |
| *c*-direction | 0.35 to 0.0016 | — |
| Electrical conductivity (single crystal) ($ohm^{-1}$ $cm^{-1}$) | | |
| *a*-direction | | |
| 30°C | $10^{-10}$ | — |
| 227°C | $10^{-7}$ | — |
| *c*-direction | | |
| 30°C | $10^{-13}$ | — |
| 227°C | $10^{-9}$ | — |
| Breakdown voltage ($V\ mil^{-1}$) | 600–700 | — |
| Dipole moment (debyes) | 2.8–3.3 | — |
| Magnetic susceptibility | $0.078\text{–}0.089 \times 10^{-6}$ | — |

The dielectric constant for anatase pigment is 48. Rutile is an electrical insulator at 68°F but its specific conductivity rises rapidly at elevated temperature, as indicated by the increased conductivity at 227°C. It is used in electronic components for its dielectric and semiconducting properties. (1)

### 4. Properties of Commercial Material

Manufactured titanium dioxide can be obtained in either the anatase or rutile crystalline form from both of the major production processes.

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1. Harry Hyman, "Working with the Volume Inorganics," Chemical Engineering/Deskbook Issue, 80 (8 October 1973) p. 23.

For the pigments, the crystal names merely denote that they have the same crystal structure as the natural minerals of those names, and do not refer to the starting material from which the pigment was produced.(1) To insure maximum light scattering the pigment must also be manufactured to the proper particle size. There are over 20 grades of rutile pigments and nearly 10 grades of anatase pigments consumed by numerous industries.

Titanium dioxide pigments are white, but there are substantial differences in hue. The rutile is more yellowish-white than the anatase, but it is higher in brightness and opacity. The pigments also are odorless, inert powders with a melting point of over 1800°C.

Titanium dioxide pigments are insoluble in organic solvents, polymers, alkalies, and all acids except concentrated sulfuric and hydrofluoric.(2)

Typical properties for the pigment form of the crystal types of titanium dioxide are described in the table below.(3)

### TABLE II

### TYPICAL PROPERTIES OF TITANIUM DIOXIDE

| | Anatase | Rutile |
|---|---|---|
| Appearance | Brilliant white powders | |
| Density ($g/cm^3$) | 3.8-4.1 | 3.9-4.2<br>4.26 (single crystal) |
| (lb/gal) | 32-34 | 33-35 |
| Refractive index | 2.55 | 2.76 |
| Oil absorption (lb/100 lb) | 18-30 | 16-48 |
| Tinting strength (Reynolds) | 1200-1300 | 1650-1900 |
| Particle size, av. (μm) | 0.3 | 0.2-0.3 |
| Hardness (moh) | 5-6 | 6-7 |
| Compressibility coefficient ($10^{-6}$ $cm^2$ $kg^{-1}$) | --- | 0.53-0.58 |
| Melting point (°C) | decomposes | |
| In air | --- | 1830 ± 15 |
| At higher % $O_2$ | --- | 1879 ± 15 |
| Specific heat (cal $°C^{-1}$ $g^{-1}$) | 0.17 | 0.17 |
| Dielectric constant | 48 | 114 |

---

1. Kirk-Othmer Encyclopedia of Chemical Technology. Second Revised Edition Vol. 20 (New York: John Wiley & Sons, Inc., 1969) p. 397

2. The TITANOX® Product Data Book. (New Jersey: NL Industries)

3. W.A. Kampfer, op. cit., p. 3
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## 5. Principal Contaminants in Commercial Product

In the manufacture of the pigments, $TiO_2$ is modified or treated with oxides of alumina, silica, zinc oxide, or a combination of oxides. Such treatments add to the ease of processing and enhance the appearance and durability of the wide variety of products utilizing titanium dioxide. A small amount of the modifiers remain in the finished product.

Manufacturers' specifications usually show a minimum percentage of $TiO_2$ (92%, 95.8%, 97%), and a "remainder" percentage. Usually, the "remainder" is alumina ($Al_2O_3$), or a mixture of alumina and silica ($SiO_2$). Occasionally, zinc oxide (ZnO) is listed as a third "remainder," and in some formulations alumina and antimony oxide are present, with the latter additive found principally in pigments used as delustrants for synthetic fibers.

A non-pigmentary product, TITANOX® 3030, recommended by NL Industries for the preparation of titanium opacified porcelain enamel, has a typical composition:(1)

| | |
|---|---|
| $TiO_2$ | 99.4% minimum |
| Iron | 70 ppm |
| Chromium | 10 ppm |
| Vanadium | 25 ppm |

In tests of Ti-Pure® products for heavy metals associated with $TiO_2$ manufacture, conducted by Du Pont for Food and Drug Administration clearance purposes, results showed mercury content in less than 0.1 ppm. Du Pont states that no mercury based ingredients are used in the manufacture of Ti-Pure® titanium dioxide.(2)

Other impurities and waste products are discussed later. (See: p. 35-44)

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1. The TITANOX® Product Data Book. loc. cit.
2. E.I. du Pont de Nemours & Co., Pigments Dept., Materials Safety Data Sheets

## B. Chemistry

Titanium dioxide is thermally stable and is very resistant to chemical attack.

### 1. Reactions Involved in Uses

The material is used because it is essentially inert in all major applications.

### 2. Oxidation

$TiO_2$ is the oxidized state.

### 3. Hydrolysis

In water, there is essentially no hydrolysis. The tendency to form the hydrate in acid or basic medium is limited, and no $Ti(OH)_4$ form is reported. The lower hydrates of the dioxide "are not obtainable by direct addition of water to the crystalline oxides, but may be prepared in other ways. . . . They are weaker acids than carbonic acid."(1)

### 4. Photochemistry

Despite the inertness of $TiO_2$, there is some evidence that the untreated pigments can contribute to the photodegradation of organic systems when exposed to ultraviolet radiation. The pigments can be treated with the oxides of metals, such as alumina, silica, zinc, etc., in a manner which will substantially reduce their photoreactivity. Such treatment helps reduce the tendency of $TiO_2$ to chalk in organic media exposed to moisture and sunlight. The pure anatase is more active than pure rutile as a photocatalyst for the destruction of paint films. It also chalks more rapidly than the rutile and is therefore usually treated for use in this application.

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1. P.C.L. Thorne and E.R. Roberts, Inorganic Chemistry. (Fritz Ephraim) Sixth Edition Revised (Edinburgh and London: Oliver and Boyd Ltd. and New York: Interscience Publishers, Inc., 1954) p. 847

## 5. Other

Titanium dioxide is inert to most acids and alkalies, slowly soluble in hydrofluoric acid or in hot concentrated sulfuric acid.

When $TiO_2$ is heated strongly in a vacuum there is a slight loss of oxygen, accompanied by the development of a dark blue color. This loss of oxygen is insignificant and is reversible.

Hydrogen, carbon monoxide, and carbon reduce $TiO_2$ only partially at high temperatures and pressures, yielding lower oxides or mixtures of carbide (in the case of carbon monoxide or carbon) and lower oxide.

Chlorination is accomplished only in the presence of a reducing agent, the position of equilibrium in the system $TiO_2 + 2Cl_2 \rightleftarrows TiCl_3 + O_2$ being far to the left.(1)

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1. Kirk-Othmer Encyclopedia of Chemical Technology. op. cit., p. 396

## II. ENVIRONMENTAL EXPOSURE FACTORS

### A. Production and Consumption

### 1. Quantity

In 1974, the production capacity of nine U.S. $TiO_2$ manufacturers was estimated at 939,000 tons.(1) This figure represents an increase of 114,000 tons over 1973 capacity and indications are that $TiO_2$ capacity is rising.

Reported annual production figures vary, depending on time of reporting and other factors. One source gives 1972 production as 718,000 tons; 1973 production as 772,000 tons; and 1974 production as 815,000 tons. Production in 1975 is estimated at 835,000 tons.(2) These figures indicate an expected slowing in production rate.

Another source, however, sets 1972 production at 687,300 tons, and shows a continued increase in annual consumption from 1967. In 1971, apparent consumption was 723,600 tons, including imports. In 1972, it was 787,100 tons, including a much larger amount of imports -- 86,400 tons, 11% of apparent consumption. Imports, in recent years, have ranged from 5% to 10% of apparent consumption and no great change in percentage levels is anticipated in the near future. Exports have been usually less than 2% to 3% of production (about 15,000 tons) from 1966 through 1971, but declined to 10,000 tons in 1972.(3)

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1. Directory of Chemical Producers. (Menlo Park, California: Chemical Information Services, Stanford Research Institute, 1974) p. 918
2. David M. Kiefer, "U.S. Industry Girds for No-Growth Year," Chemical & Engineering News, 52 (23 December 1974) p. 20
3. U.S. Environmental Protection Agency, Economic Analysis of Effluent Guidelines for the Inorganic Chemicals Industry, EPA-230/2-74-015 (Washington, D.C.: U.S. GPO, April 1974) pp. 58-9

In 1972, the three major user industries -- paint, paper, and plastics -- accounted for almost 80% of the 787,000 tons consumed, the value of which has been reported at nearly $433 million on a delivered basis.(1)

## 2. Producers, Major Distributors, and Production Sites

The companies producing titanium dioxide in 1974, their plant locations, and their annual capacities are listed in Table III. The information is derived from the 1974 Directory of Chemical Producers. Recent changes include the purchase of Sherwin-Williams Company's Ashtabula, Ohio, plant by SCM Corporation.(2) By 1975, Du Pont anticipates that the annual capacity of its Edge Moor, Delaware, plant will be 160,000 tons/year.(3)

## 3. Production Methods & Processes

### a. Manufacture of Titanium Dioxide Pigments

Titanium dioxide, when used as a pigment, is in the form of fine particulate matter with a median particle diameter of about 0.2μ. A pigment has been defined as any particulate matter that is insoluble in, and essentially physically and chemically unaffected by, the media into which it is dispersed. Because titanium dioxide is the most widely used white pigment, the titanium dioxide pigment manufacture is central to the industry. White pigments are also used with colored materials to achieve various shades.

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1. U.S. Environmental Protection Agency, Economic Analysis of Effluent Guidelines for the Inorganic Chemicals Industry, op. cit., pp. 58, 60-1
2. "At Sherwin-Williams, Change is More Than Logo Deep," Chemical Week, 116 (5), (29 January 1975) pp. 34-5
3. "Cleaner Units for $TiO_2$ Still Leave Du Pont at Sea," Chemical Week, 116 (1), (1 January 1975) p. 26

## TABLE III(1)

## PRODUCERS OF TITANIUM DIOXIDE

| COMPANY | PLANT LOCATION | ANNUAL CAPACITY (Thousands of Tons) |
|---|---|---|
| American Cyanamid Co.<br>(Pigments Division) | Savannah, Ga. | 112 |
| Combustion Engineering, Inc.<br>(C-E Minerals Division) | Camden, N.J.<br>Wilmington, Delaware | n.a.<br>n.a. |
| E.I. du Pont de Nemours & Co., Inc.,<br>(Pigments Department) | Antioch, Calif.<br>Edge Moor, Delaware<br>New Johnsonville, Tenn. | 27<br>112<br>228 |
| Gulf and Western Industries, Inc.,<br>(The N.J. Zinc Co., Subsidiary) | Gloucester City, N.J.<br>Ashtabula, Ohio* | 43<br>27 |
| Kerr-McGee Corp.<br>(Kerr-McGee Chemical Corp., Subsidiary) | Hamilton, Mississippi | 46 |
| Lonza Inc. | Mapleton, Ill. | n.a. |
| NL Industries Inc.<br>(Titanium Pigment Div.) | St. Louis, Mo.<br>Sayreville, N.J. | 115<br>124 |
| SCM Corp.<br>(Glidden-Durkee Div.)<br>(Pigments and Color Group) | Baltimore, Md.<br>Ashtabula, Ohio(2) | 78<br>27 |
| Transelco, Inc. | Penn Yan, N.Y. | n.a. |
| | TOTAL | 939 |

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*Leased from Cabot Corporation

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1. Directory of Chemical Producers, loc. cit.
2. "At Sherwin-Williams, Change is More Than Logo Deep," loc. cit.

The methods of titanium dioxide preparation are related to the product to be produced and to the end use of material, as well as the grade, properties, and composition of the particular raw materials. Analyses of typical ores used in $TiO_2$ manufacture are shown in Table IV.(1)

Although many modifications are introduced by individual manufacturers, there are basically two processes for manufacturing $TiO_2$ -- the so-called "sulfate" and "chloride" processes. Plant capacity in the U.S. is divided almost equally between these two processes, of which the sulfate is the older. The chloride process, introduced in 1956, has received widespread acceptance because it promises: (a) reduced investment, with figures showing 60-70% of a sulfate plant; (b) lower production costs with savings up to 5-6¢ per pound; (c) better product quality; and (d) "cleaner" from an environmental aspect. Since 1956, the U.S. has built no new sulfate plants; a few have been built overseas. Table V gives the location of those companies using either the sulfate or chloride process.

### (1) Sulfate Process

The major portion of the world's titania is produced by the sulfate process. The primary raw material used is ilmenite ore or sand containing 40-60% $TiO_2$. However, some types of ilmenite are not suitable raw materials for pigment manufacture because of impurities which pass through the process to contaminate the product. There are instances where Canadian slag, containing 60-70% $TiO_2$, is substituted for ilmenite. This slag has a lower iron content and correspondingly higher titanium content than ilmenite. In general, the sulfate process employs sulfuric acid at high temperatures to separate and recover $TiO_2$ from ilmenite or slag.

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1. U.S. Environmental Protection Agency, Development Document for Effluent Limitations Guidelines...Major Inorganic Products. EPA-440/1-74-007-a (Washington, D.C.: U.S. GPO March 1974) p. 175

## TABLE IV

## ANALYSES OF TYPICAL ORES USED FOR TITANIUM DIOXIDE MANUFACTURE

| Constituent (Wt. %) | Adirondack | Australian Ilmenite | Florida Ilmenite | Australian Rutile | Slag |
|---|---|---|---|---|---|
| $TiO_2$ | 44.5 | 55.4 | 64.0 | 96.3 | 71.0 |
| $FeO$ | 38.0 | 23.8 | 3.2 | | 10.9 |
| $Fe_2O_3$ | 5.8 | 16.9 | 26.9 | 0.28 | |
| $P_2O_5$ | 0.04 | 0.08 | 0.21 | 0.03 | 0.01 |
| $V_2O_5$ | 0.14 | 0.17 | 0.13 | 0.56 | 0.5 |
| $Al_2O_3$ | 1.79 | 0.94 | 1.5 | 0.39 | 5.7 |
| $CaO$ | 0.58 | 0.02 | 0.13 | 0.01 | 1.0 |
| $MgO$ | 2.14 | 0.27 | 0.35 | 0.05 | 5.0 |
| $SiO_2$ | 2.48 | 0.15 | 0.3 | 0.28 | 5.0 |
| $MnO$ | 0.50 | 0.72 | 1.35 | 0.01 | 0.3 |
| $S$ | 0.17 | 0.01 | 0.09 | | 0.09 |
| $Co$ | 0.02 | 0.11 | | | |
| $Cr_2O_3$ | 0.01 | 0.14 | 0.10 | 0.20 | 0.2 |
| $ZrO_2$ | | | 0.07 | 0.6 | |
| $Fe$ | | | | | 0.5 |
| $C$ | | | 0.27 | | |
| $NbO_2$ | | | 0.11 | 0.30 | |
| $H$ | | | 0.27 | 0.02 | |

N.B. Blank spaces indicate low impurity level or absence of reliable analytical data.

## TABLE V(1)

### PLANT LOCATIONS WHERE SULFATE PROCESS IS REPORTEDLY USED

| COMPANY | PLANT LOCATION | ANNUAL CAPACITY (Thousands of Tons) |
|---|---|---|
| American Cyanamid Co. (Pigments Division) | Savannah, Georgia | 72 |
| Gulf and Western Industries, Inc., (The N.J. Zinc Co., Subsidiary) | Gloucester City, N.J. | 43 |
| NL Industries, Inc. (Titanium Pigment Division) | St. Louis, Missouri | 115 |
| | Sayreville, N.J. | 124 |
| SCM Corporation (Glidden-Durkee Div., Pigments & Color Group) | Baltimore, Maryland | 53 |

### PLANT LOCATIONS WHERE CHLORIDE PROCESS REPORTEDLY IS USED

| COMPANY | PLANT LOCATION | ANNUAL CAPACITY (Thousands of Tons) |
|---|---|---|
| American Cyanamid Co. (Pigments Division) | Savannah, Georgia | 40 |
| E.I. du Pont de Nemours & Co., Inc. (Pigments Department) | Antioch, California | 27 |
| | Edge Moor, Delaware | 112* |
| | New Johnsonville, Tenn. | 228 |
| Gulf and Western Industries, Inc., (The New Jersey Zinc Co., Subsidiary) | Ashtabula, Ohio** | 27 |
| Kerr-McGee Corp. (Kerr-McGee Chemical Corp., Subsidiary) | Hamilton, Mississippi | 46 |
| SCM Corporation (Glidden-Durkee Div., Pigments & Color Group) | Baltimore, Maryland | 25 |
| | Ashtabula, Ohio(2) | 27 |

---

* By 1975, annual capacity is expected to be 160,000 tons/year.(3)

** Leased from Cabot Corporation

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1. *Directory of Chemical Producers*. *loc*. *cit*.
2. "At Sherwin-Williams, Change Is More Than Logo Deep," *loc*. *cit*.
3. "Cleaner Units for $TiO_2$ Still Leave Du Pont at Sea," *loc*. *cit*.

The amount of acid required for this process ranges from 2.5 to 4.5 pounds per pound of finished pigment, depending on the $TiO_2$ content of the ore.$^{(1)}$ An acid solution of titanyl sulfate results as an intermediate product. The acid solutions are clarified, cooled, and sent to a vacuum crystallizer where a portion of the ferrous sulfate crystallizes out and is separated by centrifugation. This salt can be sold or disposed of as a waste. There are exothermic reactions which proceed rapidly causing a temperature increase from 125 to 200°C. The reactions are carried on continuously or as a batch process.$^{(2)}$

$$FeTiO_3 + 3H_2SO_4 \rightarrow Ti(SO_4)_2 + FeSO_4 + 3H_2O$$

$$FeTiO_3 + 2H_2SO_4 \rightarrow TiOSO_4 + FeSO_4 + 2H_2O$$

In the essential step, the titanium sulfate is hydrolyzed to form a white, nonpigmentary hydrate. The addition of water converts the titanium portion of the salt to metatitanic acid, which precipitates.

$$TiOSO_4 + 2H_2O \rightarrow TiO_2 \cdot H_2O + SO_4$$

The hydrate is then calcined at temperature up to 1250°C to remove the water and absorbed sulfur trioxide to form crystalline titanium dioxide.

$$TiO_2 \cdot H_2O + \text{Heat} \rightarrow TiO_2 + H_2O$$

Finally, the $TiO_2$ is milled, surface treated (as needed) and packaged for sale. The final chemical form of the $TiO_2$ pigment, anatase or rutile, is determined by the nucleus crystal used in the seed precipitation in the hydrolysis step.

One of the major disadvantages of the sulfate process is the resultant large amounts of waste in the form of spent sulfuric acid and ferrous sulfate (copperas).

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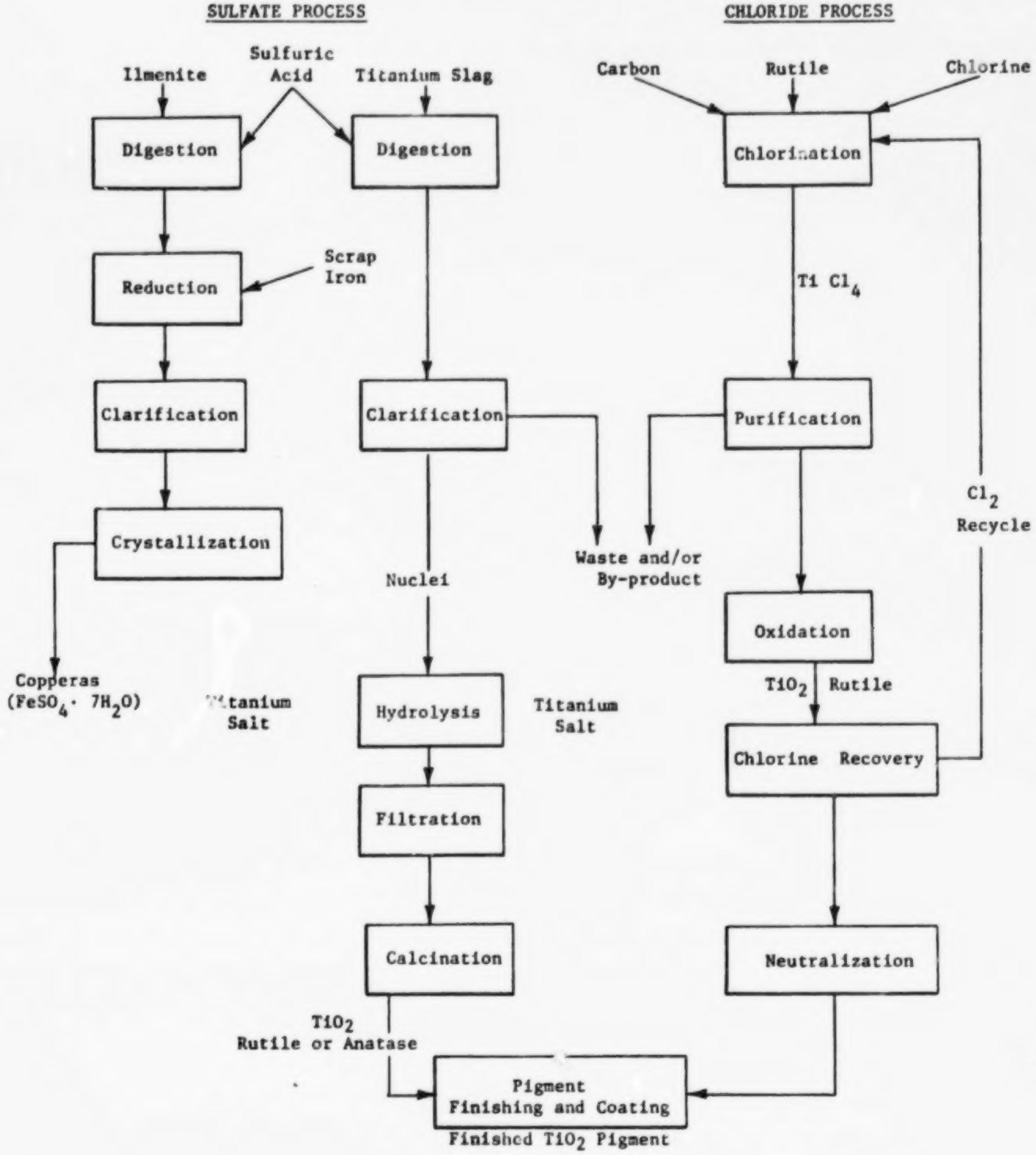
1. U.S. Environmental Protection Agency, Economic Analysis of Effluent Guidelines for the Inorganic Chemicals Industry. op. cit., p. 64
2. Kirk-Othmer Encyclopedia of Chemical Technology. op. cit., pp. 351-2

FIGURE I

$TiO_2$ PIGMENT MANUFACTURING PROCESSES


SULFATE PROCESS
CHLORIDE PROCESS
Ilmenite
Sulfuric Acid
Titanium Slag
Carbon
Rutile
Chlorine
Digestion
Digestion
Chlorination
Reduction
Scrap Iron
Ti Cl$_4$
Clarification
Clarification
Purification
Cl$_2$ Recycle
Crystallization
Nuclei
Waste and/or By-product
Oxidation
Copperas (FeSO$_4$· 7H$_2$O)
Titanium Salt
Hydrolysis
Titanium Salt
TiO$_2$ Rutile
Chlorine Recovery
Filtration
Calcination
Neutralization
TiO$_2$ Rutile or Anatase
Pigment Finishing and Coating
Finished TiO$_2$ Pigment

## (2) Chloride Process

The chloride process for titanium dioxide manufacture was introduced in the U.S. by Du Pont in 1958. In this process, rutile ores containing 90 to 97% $TiO_2$ are reacted with chlorine over carbon or coke, as a reducing agent, to produce titanium tetrachloride. The various oxides in the ore are vaporized at a furnace temperature of 850° to 1,250°F and leave the furnace in a gaseous state.(1)

$$TiO_2(+Fe_2O_3) + 2Cl_2 + C \rightarrow TiCl_4 + CO_2(+FeCl_3)$$

This process is attractive because the $TiCl_4$ may be produced in a high degree of purity.

Either hydrolysis of $TiCl_4$ or oxidation in the vapor phase is used to produce $TiO_2$. Hydrolysis may be accomplished with water vapor to produce $TiO_2$ and HCl, or liquid water to produce titanic acid, $H_2TiO_3$, and HCl. The titanic acid is then precipitated and ignited to produce $TiO_2$.

$$TiCl_4 + 2H_2O \rightarrow TiO_2 + 4HCl$$

In oxidation, purified $TiCl_4$ is fed to a reaction chamber with air or oxygen. The resultant smoke is fine particles of $TiO_2$ in an atmosphere of chlorine (along with nitrogen if air is used.) The $TiO_2$ is collected and the chlorine is recycled. This reaction is exothermic and is carried out continuously at about 1000°C.(2)

$$TiCl_4 + O_2 \rightarrow TiO_2 + 2Cl_2$$

Recycling the chlorine makes the oxidation process economically attractive. Furthermore, Du Pont has developed the capability of using ilmenite in its chloride process which helps lower its raw material costs.

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1. W.L. Faith, D.B. Keyes, and R.L. Clark, Industrial Chemicals. Third Edition (New York: John Wiley & Sons, Inc., 1965) p. 765

2. Kirk-Othmer Encyclopedia of Chemical Technology. op. cit., p. 351

Impurities in the chloride system, such as iron and other metal chlorides, entrained coke and ore, carbon monoxide, carbon dioxide, and hydrogen chloride must be removed prior to the oxidation reaction to take care of effluent waste control problems.(1)

## 4. Market Price

The market prices of titanium dioxide ore depend to a large part on the type of ore and its percentage of $TiO_2$ content. An example of the broad price variations is given below. It is taken from 1970 data.(2)

TABLE VI

$TiO_2$ Content and Prices for Four Types of Titanium Ore

| Ore | Content $TiO_2$ (%) | Approximate Price ($/short ton) As Ore | Approximate Price ($/short ton) As 100% $TiO_2$ |
|---|---|---|---|
| Ilmenite | 45 | 20 | 44 |
| Ilmenite concentrate | 60 | 33 | 56 |
| Titanium slag | 70 | 45 | 64 |
| Rutile | 96 | 160 | 167 |

Bulk prices have risen dramatically to over $125 to $150 per ton from an average price of $80-85 per ton in the late 1950's.(3)

By mid-1973, the purchase price for dry-milled anatase was about 24 cents per pound and for wet-milled was around 28.5 cents per pound. Recent price hikes have been attributed to rising production and pollution control costs.(4)

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1. U.S. Environmental Protection Agency, Development Document for Effluent Limitations Guidelines...Major Inorganic Products. op. cit., p. 55

2. W.A. Kampfer, op. cit., p. 11
Copyright © 1973, John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

3. Nicholas R. Iammartino, "Troubled Times for $TiO_2$," Chemical Engineering, 79 (1 May 1972) p. 35

4. "American Cyanamid Has Raised Titanium Dioxide Tabs," Chemical Week, 112 (28 March 1973) p. 27

Late in 1974 NL Industries increased its prices for all rutile and wet milled anatase grades of $TiO_2$ by five cents per pound and its nonpigmentary and dry milled anatase grades by three cents per pound. Thus their current prices for rutile grades range from 40 to 41 cents per pound for carloads or 20-ton minimum truckloads; 40 3/4 to 41 3/4 cents per pound for 10 to 20 tons; 42 to 43 cents per pound for 5 to 10 tons; and 43 to 44 cents per pound for less than five tons. Their current prices for anatase range from 35 to 43 cents per pound depending on the grade and for nonpigmentary grade range from 35 to 38 cents per pound. There is an additional one cent per pound charge for shipments west of the Rocky Mountains and a $15 charge for small quantities of less than 2,500 pounds.(1)

Prices for N.J. Zinc Company's anatase and rutile grades of $TiO_2$ are 43.5 cents and 38.5 cents per pound respectively. An increase of 3.5 cents per pound is scheduled to be effective as of March 1, 1975.(2) However, in March 1975, the Glidden-Durkee Division of SCM Corporation rescinded the five cents per pound increase in the price of its Zopaque $TiO_2$ products that had been announced in January. Bulk prices will remain at the July 1974 level of 40 cents per pound while there is an revision on smaller shipments as follows:(3)

| | |
|---|---|
| 5-ton lots | 1 cent/pound differential over bulk prices (down from 2 cents/pound) |
| less than 5-ton lots | 1.5 cents/pound differential over bulk prices (down from 3 cents/pound) |

The prices of anatase pigment has increased about 6 1/2 cents per pound over the last twenty years, rutile by about 7 cents per pound, 30% extended $TiO_2$ pigment by 2 1/2 cents per pound, and 50% extended $TiO_2$ pigment by 1 3/4 cents per pound.(4) The greatest increase, however, occurred in the early and middle 1950's.

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1. "Titanium Dioxide," Rubber Age, 106 (December 1974) p. 12
2. "Titanium Dioxide," Rubber Age, 107 (February 1975) p. 14
3. "Pigments," Rubber Age, 107 (March 1975) p. 12
4. W.A. Kampfer, op. cit., p. 9

Table VII shows the smoothing out of the list prices from 1965 through 1971. Commercial shipment values of titanium dioxide are also given in that table.(1)

## TABLE VII

### $TiO_2$ COMMERCIAL SHIPMENT VALUES
(Shipments in Thousands of Tons)

| | Commercial Shipments | Total Value[1] | Value/Lb.[2] | List Prices[3] | |
|---|---|---|---|---|---|
| | | | | Anatase | Rutile |
| 1965 | 524.5 | 274.7 | .261 | .25 | .26 |
| 1966 | 545.4 | 279.7 | .256 | .25 | .26 |
| 1967 | 542.6 | 277.2 | .255 | .25 | .26 |
| 1968 | 564.4 | 288.8 | .256 | .25 | .26 |
| 1969 | 590.1 | 301.1 | .255 | .26 | .27 |
| 1970 | 560.9 | 277.8 | .248 | .26 | .27 |
| 1971 | 581.2 | 262.4 | .226 | .26 | .26 |

[1] Value in \$ Millions.

[2] Value in \$ per Pound.

[3] Car lot, \$ per Pound.

Source: Current Industrial Reports, U.S. Department of Commerce.

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1. U.S. Environmental Protection Agency, Economic Analysis of Effluent Guidelines for the Inorganic Chemicals Industry. op. cit., p. 78

## 5. Market Trends

In 1974, there were nine producers of $TiO_2$ in the U.S. with fifteen plants in operation, only one of which is in the western portion of the country.(1) Although both the sulfate process and the chloride process are being employed, new titanium dioxide pigment plant construction since 1956 has been chloride facilities with capacities between 25 to 30,000 tons. Du Pont, the company responsible for introducing the chloride process initially, is increasing the capacity of its New Johnsonville, Tennessee, plant to 195,000 tons (scheduled for completion year-end 1973) and is actively considering a new 100,000 ton chloride facility in Georgia.(2) Furthermore, Du Pont Pigments Department stated in the Fall of 1974 that when it completes its construction program at Edge Moor and other locations, it will have about doubled its output of titanium dioxide in this decade to well over a half-million tons a year.(3) Although the overall growth in titanium dioxide production has been generally and steadily up and is expected to increase into 1975, there are signs of a slowing:(4)

| | |
|---|---|
| 1972 | 718,000 tons |
| 1973 | 772,000 tons |
| 1974 | 815,000 tons |
| 1975 | 835,000 tons |

It is felt in some sectors, however, that demand could catch up to current capacity as early as 1976.

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1. Directory of Chemical Producers. loc. cit.

2. U. S. Environmental Protection Agency, Economic Analysis of Effluent Guidelines for the Inorganic Chemistry Industry. op. cit., p. 66

3. "Progress in Pigments Comes From Du Pont," Chemical Week, 115 (20 November 1974) p. 1

4. David M. Kiefer, loc. cit.

### a. Raw Materials and Market Trends

Along with production of titanium dioxide, market price bears an influence on market trends. The stability of the titanium dioxide market price depends greatly on the ready supply of raw materials. The more abundant ilmenite ores can be used to feed the sulfate process while the supply of rutile ore, which feeds the chloride process, is in question. The supply and cost of rutile have been considered factors influencing the closing or possible closing of two plants -- one being PPG Industries' Natrium, West Virginia chloride plant in 1971 and the other NL Industries' Sayreville, N.J. chloride plant.(1) Thus, one of the major and current concerns to the $TiO_2$ industry is the availability of raw materials.

Extensive deposits of ilmenite are found throughout the world. It is mined extensively in many countries, the biggest producers being the United States, Australia, and Norway. World production, since 1967, has been approximately 3 million short tons per year, with the U.S. contributing about 700,000 short tons to this total.

Known reserves of rutile, which is mined principally in Australia, are considered limited and barely able to meet demand. No rutile is mined in the United States. Current world production of about 400,000 long tons per year will probably deplete known reserves within 20-25 years. Because no new deposits of natural rutile have been found, $TiO_2$ manufacturers must seek sources of rutile other than the natural ores.

Ilmenite is ferrous titanate, $FeO \cdot TiO_2$ or $FeTiO_3$, usually containing some ferric ion, and sometimes occurring associated with other ores. It occurs massive in some areas of the world; as a constituent of beach sands in other areas. In these latter areas, the action of waves and/or wind causes a degree of concentration in the ore, which is also altered by oxidation and leaching. The result of these actions is an increase

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1. Nicholas R. Iammartino, op. cit., pp 34-6

in the ratio of ferric to ferrous iron, and a decrease in the amount of iron present with a corresponding increase in the amount of $TiO_2$. This form of titanium dioxide also changes, passing through a leucoxene stage to rutile.(1) Leucoxene is still too high in iron content for economic use in chlorine processes that depend on availability of rutile ore. In addition some types of ilmenite are unsuitable for pigment manufacture because of impurities which pass through the process to contaminate the product.

The relative abundance of ilmenite compared to rutile makes beneficiation of ilmenite promising technology.(2) One potential source to offset the question of rutile reserves is the upgrading of ilmenite to over 90% $TiO_2$ through the removal of iron. It can then be processed, utilizing the rutile chloride technology. This removal of part or all of the iron content of the ilmenite ore whereby there remains a product soluble in sulfuric acid, or which can be chlorinated economically, is the nature of the beneficiation process. Some ilmenite producers and rutile consumers alike are interested in beneficiation. Furthermore, Du Pont has a process to use mixed ores in their feed and still other manufacturers are developing technology so that unbeneficiated ilmenite can be chlorinated.

The initial trend away from sulfate to chloride manufacture of $TiO_2$ was due in part to the introduction and development of the chloride process and further reinforced by environmental questions surrounding the sulfate process. However, the chloride process is not trouble free. There are examples of investment, economic and maintenance difficulties in a few chloride plants that illustrate expenses and down-time well beyond initial estimates. The possibility of raw materials problems for the chloride plants and the development of pollution control facili-

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1. Kirk-Othmer Encyclopedia of Chemical Technology. op. cit., p. 398
2. Ibid., p. 399

ties for sulfate plants may shift the emphasis and concern regarding current dilemmas facing the $TiO_2$ manufacturer. "Although estimates indicate that the cost of chloride process plants is only 60 to 70% that of sulfate plants, the chloride process requires 96% rutile $TiO_2$ ore at about $160/ton compared to about $33/ton for ilmenite concentrate containing 60% $TiO_2$. Present day economics appear to favor the modern automated sulfate plant (with controlled emission and by-product utilization) for the production of a titanium dioxide that is completely equivalent to the chloride product."(1)

### b. Waste Disposal and Market Trends

Of the two methods of manufacturing $TiO_2$, the older sulfate process is considered to be plagued with environmental troubles. Waste disposal problems center around the spent sulfuric acid and copperas ($FeSO_4 \cdot 7H_2O$). For the most part wet scrubbers reduce the air pollution problems resulting from the particulates emitted from sulfate manufacture. Technology exists for the recovery of copperas, a portion of which is sold as a flocculating agent, with the remainder either being stockpiled or disposed of with the acid waste.

On the other hand, the chloride process is reputed to have simpler waste disposal requirements than the sulfate process. The primary reason for this is that rutile ore is the customary raw material in the chloride manufacture of $TiO_2$. Since the starting ore contains a high percentage of $TiO_2$, there is a minimum of iron chloride by-product and waste.

With the dwindling known supply of rutile, however, comes the question of modifying existing chloride plant technologies for $TiO_2$ manufacture to accommodate other feed, such as beneficiated ilmenite or to chlorinate unbeneficiated ilmenite. An acid-leaching process for ilmenite beneficiation seems to be the one most used commercially. Existing plant capacities are shown in Table VIII. Waste disposal is a limiting factor with ilmenite beneficiation, as is iron oxide pulp tailing.(2)

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1. W.A. Kampfer, op. cit., p. 12
2. Nicholas R. Iammartino, op. cit., p. 35

## TABLE VIII

## PLANT LOCATIONS AND CAPACITIES FOR ILMENITE BENEFICIATION BY ACID-LEACHING PROCESS

| COMPANY AND PLANT LOCATION | CAPACITY BENEFICIATED ILMENITE |
|---|---|
| Gulf Chemical and Metallurgical Corporation<br>Texas City, Texas | *40,000 tons/yr. |
| Western Titanium N.L.<br>Australia | **12-13,000 tons/yr. |
| Benilite Corporation of America<br>Corpus Christi, Texas | 2,000 tons/yr. |

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* limited by waste disposal problems to 10,000 tons/yr. in 1971

** with some $Fe_3O_4$ pulp tailing

Other beneficiation technologies follow different routes, such as those shown in Table IX below:(1)

## TABLE IX

## PROCESSOR AND TYPE OF PROCESS USING OTHER BENEFICIATION TECHNOLOGY

| PROCESSOR AND LOCATION | TYPE OF PROCESS AND YIELD | BASIC TECHNOLOGY |
|---|---|---|
| U.S. Bureau of Mines<br>Albany, Oregon | pyrometallurgical process with 90-97% $TiO_2$ concentrate selling for over $80/ton and marketable pig iron | oxidation and fluxing of ilmenite slag in electric furnace |
| Rolla Metallurgy<br>Research Center<br>Rolla, Missouri | carbonyl process | iron penta-carbonyl by-product can be decomposed to iron powder and CO (for recycle) |
| CSIRO and<br>Murphy Ores Inc.<br>Brisbane, Australia | Murso Process Product with 95-96% $TiO_2$ | oxidation and separation of iron and other impurities |

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(1) Nicholas R. Iammartino, op. cit., p. 36

## B. Uses for Titanium Dioxide

Consumption of titanium dioxide is usually divided into two general categories - the pigment industry and non-pigment uses. The coarse particle size is preferable for nonpigmentary purposes with its "ease of handling, freedom from dusting, ease of blending with other materials, and, in the ceramic industry, ease of shrinkage control during firing."(1)

On the other hand, improvements in technology over the years from about 1954 to about 1959 made it possible to produce chloride process pigments possessing superior tinting strength, hiding power, and color by virtue of their smaller particle size and narrower distribution range compared to their sulfate counterparts. More recently sulfate process pigments have been manufactured in the necessary, closely controlled particle size range that is considered the single most significant factor in the production of titanium dioxide with optimum properties.(2)

### 1. Major Uses

The distribution of titanium pigment shipments by industries is an indication of the end use pattern of the titanium dioxide produced. In 1967, the percentage distribution by gross weight was reported as listed in Table X.(3)

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1. *Kirk-Othmer Encyclopedia of Chemical Technology*. *op*. cit., p. 396
2. W.A. Kampfer, *op*. *cit*., p. 12
3. *Kirk-Othmer Encyclopedia of Chemical Technology*. *op*. *cit*., p. 408

## TABLE X

## PERCENTAGE DISTRIBUTION OF TITANIUM PIGMENT SHIPMENTS BY INDUSTRIES

| Industry | % (Distribution by Gross Wt.) |
|---|---|
| paints, varnishes & lacquers | 61.9 |
| paper | 14.6 |
| floor coverings | 2.7 |
| rubber | 2.8 |
| coated articles & textiles (oil cloth, shade cloth, artificial leather etc.) | 1.4 |
| printing ink | 2.0 |
| roofing granules | 1.1 |
| ceramics | 1.9 |
| plastics (except floor coverings and vinyl-coated fabrics and textiles | 5.1 |
| other (including export) | 6.5 |

The percentage distribution of $TiO_2$ in total pigment used by the two principal industries at that time was:

| Industry | % (Distribution by $TiO_2$ Content) |
|---|---|
| paints, varnishes and lacquers | 57.5 |
| paper | 17.2 |

The percentages above refer to 587,995 short tons as the total U.S. production ($TiO_2$ content) in 1967.(1)

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1. Kirk-Othmer Encyclopedia of Chemical Technology. op. cit., p. 408 Copyright © 1969, John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

More recent figures are given in Table XI to show market consumption of titanium dioxide in 1970 and 1972 distributed by industries.(1)

## TABLE XI

## MARKET CONSUMPTION OF $TiO_2$ BY INDUSTRIES

| INDUSTRY | $TiO_2$ MARKET CONSUMPTION (Thousands of Tons) 1970 | 1972 |
|---|---|---|
| Paint and Coatings | 375 | 390 |
| Paper | 147 | 158 |
| Plastics | 59 | 78 |
| Rubber | 35 | 35 |
| Floor Covering | 30 | 30 |
| Printing Ink | 18 | 20 |
| Ceramics | 17 | 21 |
| Synthetic Fibers | 10 | 10 |
| Roofing Granules | 5 | 5 |
| Other | 34 | 40 |
| TOTAL | 730 | 787 |

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1. U.S. Environmental Protection Agency, Economic Analysis of Effluent Guidelines for the Inorganic Chemicals Industry. op. cit., p. 60

### a. Paints, Varnishes, Lacquers

Although paint producers consumed 66.9% of the $TiO_2$ sold in 1950 in the U.S., by 1969 paint accounted for only 54.3% of the $TiO_2$ sales. The actual quantity of $TiO_2$ utilized in coatings has steadily increased at an annual rate of growth about 4.37% per year. (1)

Both particle size and surface treatment are specially controlled with pigmentary rutile which is used primarily for opacity, color, and tinting strength. Special treatments and manufacture provide resistance to chalking and fading in organic media (paints) exposed to the weather. Enamel grades are designed for all types of gloss and semigloss architectural and industrial coatings. Dry hiding grades are designed for flat paints including oil, alkyd and latex based products.

Pigmentary anatase is generally used in exterior paints to induce chalkings and thereby promote clean-up, to maintain a white appearance as the paint weathers. In these coatings, a blue-white color is of higher priority than is opacity.

### b. Paper

The paper industry is another large user of titanium dioxide. In paper making, water dispersibility and wire retention are probably the two most important properties required of the pigment. It is treated specially to insure high solids dispersion in aqueous systems. In the paper product as a filler, interfaces between pigment and air contribute to opacity, and provide a reduction of "show-through" in printed papers.(2)

Titanium dioxide is also used in paper coatings.

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1. W.A. Kampfer, *op. cit.*, p. 12
2. *Ibid.*, p. 20

In minimum opacity applications, such as glassine waxed paper, unbleached board and specialty papers, chloride process rutile effects economies and brightness over anastase pigments. Some pigmentary rutile is designed for use in melamine laminate compositions where its resistance to ultraviolet light discoloration is outstanding. Likewise it is recommended for use in printing inks which are applied to melamine formaldehyde laminate systems and resins.(1)

Consumption of $TiO_2$ by the paper industry has increased over the last twenty years at a rate of growth of approximately 7.1% per year. A continuation in this rate of growth may be somewhat optimistic, however, in view of the increased use of fine particle size, high brightness extenders in paper manufacture.(2) Titanium dioxide will continue to be necessary for its high refractive index and opacity.

### c. Plastics, Rubber, and Floor Tile

Very fine particle size titanium dioxide pigment is necessary to produce brightness and blue tone in plastics with pigmentation ranging from 0.5 pph of resin to 15 pph.(3) Regular particle size grades are used in plastisols and some specialized areas for chalk resistance. In addition, $TiO_2$ protects polymers which can be degraded by light, as well as all types of materials packaged in plastic containers.

Although the tonnage of $TiO_2$ used by the plastics and paper industries is low compared to that consumed by the paint industry, individual plastic products may contain a higher fraction of $TiO_2$. Titanium dioxide pigment is used in polyvinyl chloride, polyethylene, polystyrene, vinyl-asbestos floor tile, etc. In plastics applications, such properties as opacity, tinting strength, wettability, low abrasion and the ease of dispersion of

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1. The TITANOX® Product Data Book. loc. cit.
2. W.A. Kampfer, op. cit., p. 12
3. Ibid., p. 20

titanium dioxide can be obtained by treating the surfaces. Thermal discoloration in the presence of certain phenol base antioxidants and ultraviolet light absorbers can be controlled in polyolefins and vinyls. Special grades of rutile pigments are designed for high temperature exposure encountered in manufacturing blown and cast film for rigid weather resistant siding, and for acrylic plastic sheet. On the other hand, special grades of anatase pigments are recommended for white side wall rubber stock.

Consumption of $TiO_2$ by the plastics industry has increased over the last twenty years at a rate of growth of approximately 10% per year. As the applications for plastic products increases, greater consumption of titanium dioxide in the plastics industry follows. There is also an increasing trend toward the utilization of pigmented plastics where paints and coatings were previously used. (1)

## 2. Minor Uses of Titanium Dioxide

The three major use industries -- paint, paper, and plastics -- account for over 80% of the $TiO_2$ pigment consumed. However, there are numerous other industries which utilize titanium dioxide.

### a. Printing Inks

Titanium dioxide pigments are used extensively in printing inks: offset, metal decorating, textile and silkscreen. High gloss pigments are used in letterpress, gravure, and spirit flexographic inks while chloride rutile pigments with high-hiding properties are applied to low-gloss water-based flexographic inks. The low abrasivity of these $TiO_2$ pigments is another property which contributes to the utilization in inks.

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1. W.A. Kampfer, op. cit. p. 12

### b. Ceramics

The coarser grades of $TiO_2$ are employed by the ceramics industry for porcelain enamels applied to sheet steel or aluminum, glass decorating enamels, glass, and glazes. They are regenerated in the proper size through precipitation or crystallization from the frit on firing the enamel. Nonpigmentary grades of $TiO_2$ are efficient ultraviolet screening agents for glass containers of all types, providing protection for food and beverages therein contained. To obtain these properties the absorption edge at the blue end of the spectrum is shifted to longer wavelengths.

### c. Textiles

Anatase is utilized more often in the textile industry as rutile, is not so soft and may cause excessive abrasion of high-speed spinning and processing equipment. Because $TiO_2$ has a very high refractive index compared to that of synthetic fiber, the pigment offers good light scattering or delustering quality to synthetic fibers.

For internal delustering, anatase $TiO_2$ is incorporated at a level of 1% to 3% into the liquid mass before extrusion into fiber.(1) For external delustering and light stability, titanium dioxide is employed with suitable organic binders in aqueous dispersions applied as coatings or dulling-agents to the final fabric, such as polyamide, polyester, acetate, or viscose.

### d. Food and Cosmetics

A highly purified grade of $TiO_2$ is approved for use in the food and cosmetic industries. One special grade has been manufactured for years for lipstick and face powder applications. Other grades have been labelled "color additive" or "food additive" in such foods as cheeses. Titanium dioxide is also approved for use in packaging materials which are in contact with foods and special toiletries.

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1. W. A. Kampfer, op. cit., p. 21

### e. Other Rutile and Anatase Pigmentary Products

The other miscellaneous industries utilizing titanium dioxide pigments include both anatase and rutile applications. The extensive list includes cement base coatings, caulking compounds, roof granules, leather and shoe dressings and finishes for other leather products, ceiling tile and ceiling tile coatings, and welding rod coatings, to name a few.(1)

### f. Other Predispersed and Nonpigmentary Applications

Predispersed titanium dioxide is stable in hard water and compatible with calcium carbonate extenders. Examples of typical applications are gloss and semigloss latex finishes, filler and coatings for some paper makers, aqueous flexographic inks where full gloss coating is needed.(2)

Other nonpigmentary uses include particular ceramic applications. Special grades of titanium dioxide impart acid resistance to aluminum and glass label enamels and to dry process enamels for cast iron, porcelain enamels and glazes. Others aid in smelting fast fire glazes, as well as contributing high opacity. Electrical ceramic specialty applications include thermistors and capacitors and space applications.(3)

### g. Gems for Jewelry

Large titanium dioxide crystals with their translucent water-white or yellowish cast are suitable for use in jewelry. A substantially pure and massive single crystal of rutile has the properties of a precious gem with a very light straw color and with reflectance, refraction and brilliance measuring greater than those of a diamond.(4) However, the hardness of diamonds is lacking in $TiO_2$ crystals, and this is not a large use.

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1. W.A. Kampfer, *op. cit.*, p. 22
2. *TITANOX® Product Data Book*. *loc. cit.*
3. *Loc. cit.*
4. *The Merck Index*. Eighth Edition (Rahway, N.J.: Merck & Co., Inc., 1968) p. 1054

### 3. Discontinued Uses

No information was found.

### 4. Projected or Proposed Uses

No information was found.

### 5. Possible Alternatives to Uses

Only in the paper industry is the consumption of $TiO_2$ threatened by substitute products. Although it is an effective opacifier, it is at a cost disadvantage to alumina and silica clays, some of which offer nearly equivalent brightness.

To the plastics and rubber industries $TiO_2$ offers the best combination of white pigment cost, dispersability, and resistance to discoloration.

In the paint industry no equally effective white pigment in terms of hiding power has been found in years of extensive research. Titanium dioxide is also considered a key to the current trend of one-coat paint applications.

There are no apparent substitute products which are currently competitive in any of the other product application areas.

The captive consumption of $TiO_2$ pigment is in the paint industry where three out of the top six have their own pigment plants and where captive use as a percentage of apparent consumption has risen from 8% in 1965 to 14% in 1971. Du Pont, SCM Corporation's Glidden-Durkee Division, and NL Industries are major so-called "captive" users of titanium dioxide. (Sherwin-Williams no longer appears on that list with the purchase by Glidden-Durkee of the Sherwin-Williams' Ashtabula, Ohio, Plant.)(1)

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1. "At Sherwin-Williams, Change is More Than Logo Deep," loc. cit.

## C. Potential Sources of Environmental Contamination

### 1. General

Researchers, producers, and users throughout the titanium dioxide industry have given consideration to the environmental contamination potential from $TiO_2$. Principal contaminants to the environment are associated with the impurities resulting from titanium dioxide raw materials processing and the disposal of process waste. There has been considerably less environmental attention given to the transport, packaging, storage and usage of titanium dioxide.

Titanium dioxide is purchased in volumes, which are comparable to those of some commodities, but in terms of marketing, it is more like a specialty chemical than a commodity. It is utilized in numerous products for its enhancing properties. However, it retains its chemical and physical stability in end-use products.

### 2. Potential Environmental Contamination from Production

Each of the two processes for manufacturing titanium dioxide are based on somewhat different raw materials and involve quite different technologies. Consequently, each process is discussed separately below from the point of view of environmental contamination.

#### a. Potential Environmental Contamination from the Sulfate Process

As mentioned in the earlier discussion concerning the sulfate process, there are contaminants which are generated from the metallic impurities in the ilmenite ore, as well as pollutants resulting from the chemical processing of the raw materials into $TiO_2$. Silica, coke or carbon, and other sulfuric acid insoluble ore residues result from the sulfate process.

The acid wastes, however, from the sulfate processing, are of concern. The technology exists to recover sulfuric acid from the waste, but the general opinion held by those who have attempted it is that it is not economically feasible to handle the acid problem in this manner. Therefore, the acid wastes must be neutralized to meet water quality standards. Following neutralization, there results large amounts of waste products, including iron oxides or hydroxides and trace amounts of hydroxides of manganese and chromium.

A list of raw wastes, which have come from typical plant manufacture of $TiO_2$ by the sulfate process is given in Table XII below.(1)

### TABLE XII

### SULFATE PROCESS WASTE STREAMS IN TITANIUM DIOXIDE MANUFACTURE

| | | |
|---|---|---|
| 1. Dissolving and Filtration | Ore and scrap iron plus flocculants | 0.07 x total ore and scrap iron discharged |
| | $H_2SO_4$ | 0.0016 x ore |
| | Organic Carbon | 0.0004 x ore plus 0.1 x C in ore |
| 2. Copperas (if produced) | $FeSO_4.7H_2O$ (as Fe) | ($Fe^{+2}$ + 1.50 $Fe^{+3}$) in ore minus 0.33 x $TiO_2$ in ore |
| | Total Sulfate | 1.76 x iron in copperas |
| 3. Strong Acid | $FeSO_4$ (as Fe) | 0.67 x (iron in ore minus iron in copperas) |
| | $H_2SO_4$ | 1.07 x ore |
| | Other ore impurities | 0.67 x impurities in ore |
| | $TiO_2$ | 0.03 x $TiO_2$ in ore |
| | Organic Carbon | 0.0022 x ore plus 0.81 x C in ore |
| 4. Weak Acid | $FeSO_4$ (as Fe) | 0.33 x (iron in ore minus iron in copperas) |
| | $H_2SO_4$ (Total) | 0.53 x ore plus 0.25 x $TiO_2$ in ore |
| | Other ore impurities | 0.33 x impurities in ore |
| | $TiO_2$ | 0.02 x $TiO_2$ in ore |
| | Organic Carbon | 0.00025 x ore plus 0.09 x C in ore |
| 5. Vent and Kiln Scrubbing | $H_2SO_4$ | 0.01 in ore |
| 6. $TiO_2$ Losses | $TiO_2$ | 0.016 x $TiO_2$ in ore |
| | $Na_2SO_4$ | 0.03 x $TiO_2$ in ore |

Note: Effluents also contain traces of Pb and Cu from process equipment. Silica and zircon do not react and are discharged with the sludge.

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1. U.S. Environmental Protection Agency, Development Document for Effluent Limitations Guidelines...Major Inorganic Products. op. cit., p. 174

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Following the digestion of ilmenite ore in processing with concentrated sulfuric acid (about 150% of the weight of the ore), resulting sulfates of titanium and iron are leached from the reaction mass with water. In the next step, any ferric salts present are reduced to ferrous by treatment with iron scrap to prevent coloration of the final $TiO_2$ product. The resultant solutions are clarified and cooled. Ferrous sulfate (copperas), which is crystallized and separated by centrifugation, is either sold (generally as a flocculating agent) or disposed of as a solid waste.(1)

The effluents from four titanium dioxide plants which utilize the sulfate process are listed below in Table XIII and show considerable variation from plant to plant.(2) It is noted that none has a pH discharge in the 6.-9.0 range for all streams. All contain 3000 mg/l dissolved solids.

### TABLE XIII

### PARTIAL DISCHARGE DATA FROM $TiO_2$ SULFATE PLANTS

|  | Plant 142 Streams (2) |  | Plant 046 Streams (3) |  |  | Plant 122 Streams |  |  | Plant 008 |
|---|---|---|---|---|---|---|---|---|---|
| Paramater* | No.1 | No.2 | No. 1 | No. 2 | No. 3 | No. 1 | No. 2 | No. 3 | No. 1 |
| BOD$_5$ | 10 | 3 | 6 | 3 | -- | -- | 0.3 | 0.5 | -- |
| COD | 71 | 145 | -- | -- | -- | 287 | 42 | 27 | -- |
| pH | 8.0 | 1.2 | 6.5 | 5.6 | -- | 1.0 | 2.6 | 5.0 | 5 min |
| Alkalinity | 220 | -- | -- | -- | -- | -- | -- | -- | -- |
| Total Dissolved Solids | 1660 | 22,371 | 15,316 | 21,300 | 14,000 | 15,400 | 3,000 | 2,700 | 5,000 |
| Iron | 0.02 | 823 | 0.5 | 1.7 | 31,000 | 1,000 | 45 | 15 | 100 |
| Sulfate | 1,170 | 12,377 | 1,617 | 1,378 | 131,000 | 6,800 | 187 | 125 | -- |
| Chloride | 51.5 | 105 | 6,394 | 7,900 | -- | 625 | 2,480 | 2,830 | -- |
| Acidity | -- | 11,435 | 36 | -- | -- | 20,000 | 160 | 1000 | -- |
| Flow, cu m/day | 10,200 | Combined | 20,000 | 123,400 | 6,100 | 20,000 | 40,900 | 30,300 |  |
| (MGD) | (2.7) | -- | (5.5) | (32.6) | (1.6) | (5.5) | (10.8) | (8.0) |  |

(1) One plant of one manufacturer is not listed here. Data on titanium dioxid and chromate concentrations were provided.

(2) The corporation owning this facility is currently developing a process for recovery and recycle of the sulfuric acid used. This process is still under testing on the pilot plant scale.

(3) This plant barges its strong acid wastes out to sea for disposal. This method of disposal of highly acid wastes containing large amounts of dissolved heavy metals is not considered satisfactory. Effluent No. 3 is the available data on material dumped at sea.

*mg/l unless otherwise specified

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1. U.S. Environmental Protection Agency, Development Document for Effluent Limitations Guidelines...Major Inorganic Products. op. cit., p. 173

2. Ibid., p. 179

### b. Potential Environmental Contamination from the Chloride Process

As mentioned in the earlier discussion concerning the chloride process, titanium dioxide ores are chlorinated, using coke to promote the reaction, to produce titanium tetrachloride (as an intermediate) plus carbon dioxide and iron chloride. In the next step, the titanium tetrachloride is oxidized to $TiO_2$ and chlorine, which is recycled.

Carbon, unreacted ore, and some non-volatile chlorides of metallic impurities in the ore, result from the chlorination and are considered non-hazardous. The products of chlorination are cooled and the undesired metal chlorides condensed.(1) The solid waste stream, however, usually contains titanium hydroxide and small amounts of compounds of vanadium, aluminum, copper, chromium, zirconium, and niobium. The use of copper is not considered representative of the industry, but where added in the purification stage, it will be the major constituent in the waste.

### c. Potential Contamination from Titanium Dioxide Plants

Waste discharge data for nine titanium dioxide plants are summarized in Table XIV. The information therein was obtained from both discharge permit applications and data sheets. The parameter 'loadings' were calculated from reported daily average concentrations, discharge flow rates and annual production rates. The computation for each plant was made for 350 days operation during the year. Of the nine plants, four use the chloride process only, three use the sulfate process only and two use both processes. Three of the plants in this group dispose of part of their wastes in landfills, two discharge part in the ocean by barge transport and one uses deep-well injection. For six of the plants, the data

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1. U.S. Environmental Protection Agency, Development Document for Effluent Limitations Guidelines...Major Inorganic Products. op. cit., p. 53

represent the total discharge of plant effluents to streams and to landfill, deep well, or ocean. For the other three plants, the data given in the Table represent only a part of the total wastes. Although the treatment of wastes discharged to streams varies considerably, all of the nine plants reported that their waste disposal systems were in the process of being modified or improved.(1)

## TABLE XIV(2)

## WASTE DISCHARGE DATA FOR TITANIUM DIOXIDE PLANTS[a]

| Parameter | Waste loading, kg/metric ton of product[b,c] | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Plant A<br>Cl, $SO_4$ | Plant B<br>$SO_4$ | Plant C[d]<br>Cl, $SO_4$ | Plant D[d]<br>$SO_4$ | Plant E[d]<br>Cl | Plant F<br>Cl | Plant G<br>Cl | Plant H<br>Cl | Plant I<br>Cl, $SO_4$ |
| Average wastewater discharge, millions of liters/day | 112 | 35.2 | 135 | 146 | 11.0 | 134 | 2.8 | 2.6 | 109 |
| Total dissolved solids | 2,650 | 2,274 | 3,720 | 7,240 | 601 | 1,330 | 175 | 169 | - |
| Total suspended solids | 46 | 24 | 53 | 595 | 7.1 | 15 | - | 0.2 | - |
| Total volatile solids | 1,043 | - | - | 1,060 | - | - | - | 4.4 | - |
| Acidity/alkalinity | 1,652 | - | - | 20 | 15 | - | - | 2.2 | - |
| $BOD_5$ | 4.6 | 0.6 | 0 | 2.1 | 0.6 | - | - | <0.4 | - |
| COD | 40 | 26 | 28 | - | 9.1 | - | - | 1.1 | - |
| Oil and grease | 3.3 | 0 | 0 | - | <0.1 | - | - | - | 1.0 |
| Total organic carbon | 1.5 | - | - | 2.2 | 3.5 | - | - | 0.6 | 2.0 |
| Total organic nitrogen | 1.0 | 1.3 | 0 | 1.4 | 0.3 | - | - | 0.01 | 0.6 |
| Ammonia, as N | 0.4 | 7.7 | 0 | <0.1 | 0.7 | - | - | <0.01 | - |
| Chloride | 316 | 13 | 35 | 3,540 | 453 | 877 | 181 | 47 | 853 |
| Fluoride | - | - | - | - | 0.2 | - | - | 0.05 | 0.2 |
| Nitrate | - | - | - | - | - | - | - | 0.05 | - |
| Sulfate | 484 | 980 | 3,170 | 205 | 32 | 26 | 35 | 16 | 486 |
| Sulfide | - | - | 1.0 | <0.03 | 0.008 | - | - | <0.02 | 0 |
| Phosphorus, total | 0.2 | 0.5 | 0.06 | 0.05 | 0.2 | - | - | 0.002 | - |
| Iron | 449 | 656 | 192 | 7 | 0.05 | 330 | 27 | 11 | 144 |
| Titanium | 26 | 19 | 40 | 0.9 | 9.8 | - | 1.4 | <0.02 | 25 |
| Antimony | 300 | - | - | - | - | - | - | 20 | - |
| Arsenic | - | - | - | - | - | - | - | 10 | 20 |
| Cadmium | 3 | 0 | - | <1 | <0.6 | - | - | <2 | 0 |
| Chromium | 440 | 1,100 | 1,900 | 30 | 50 | - | 0.2 | 1,800 | 800 |
| Lead | 150 | 0 | 200 | <0.3 | 3 | - | - | <0.4 | 0 |
| Manganese | 14,000 | - | - | - | - | - | - | 0.4 | 4,000 |
| Mercury | 0.04 | 0 | 0 | <0.3 | <0.1 | - | 0.02 | <0.02 | 0 |
| Nickel | - | - | - | - | 10 | - | 1 | - | 90 |
| Selenium | 500 | - | - | - | <0.6 | - | - | - | - |
| Zinc | 600 | 1,100 | 600 | 40 | 3 | - | - | 2,100 | 700 |

[a] Data from Corps of Engineers discharge permit applications and data sheets.

[b] A zero indicates that the constituent was reported as "absent" or "not detected"; a dash indicates that no information was reported on the concentration of the constituent.

[c] Waste loadings for the ten metals listed in the lower part of the table are in g/metric ton of product.

[d] Plants C, D, and E dispose of part of their wastes by methods other than discharge to streams, but did not provide data on these disposal methods. The data given for these plants represent only discharges to streams.

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1. Southern Research Institute, Waterborne Wastes of the Paint and Inorganic Pigments Industries. EPA-670/2-74-030, PB-232 019, (Springfield, Virginia: NTIS, March 1974) p. 36

2. *Ibid.*, p. 40

### d. Air Pollution

In both the chloride and sulfate processes, gases are treated to recover valuable constituents for recycle, especially chlorine and product dusts. Although complete removal of all gaseous pollutants is rarely possible, the magnitude of the gaseous emissions should be small when compared with the control of fine particulates. As with all particulate removal processes, the installation of air pollution control devices depends upon either recovery of an economically valuable product or a threat of penalties from regulatory agencies for failure to meet emission standards. Although technology is available to remove large size particulates, many processes such as encountered in the manufacture of titanium dioxide generate fumes or smokes which have particulate sizes approaching the size of molecules which make their collection very difficult or impossible.

The nature of titanium dioxide emissions is largely dependent on its boiling point (given at 2700°C). Because it is substantially higher than the combustion temperatures of coal or incinerator refuse, the emission in both cases, is probably physically and chemically the same as the feed material.(1)

Fine particles (1 micrometer in diameter and smaller) from $TiO_2$ emissions may travel considerable distances before being deposited or being washed out of the air by natural processes. Hard-rock mining of ilmenite produces particles ranging from 1/2 to 10 micrometers in diameter with an average diameter of approximately 5 micrometers.(2) Furthermore, since ilmenite is a moderately hard material, the beneficiating operations, which involve intense mechanical pulverization, result in a moderate amount of fine particles.

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1. GCA Corporation, Emissions Inventory of Sources and Emissions of Titanium. EPA-450/3-74-208 (Research Triangle Park, N.C.: U.S. EPA, May 1973) p. 27

2. *loc. cit.*

About 9.8% of total U.S. $TiO_2$ emissions comes from pigment handling processes, including incineration of paper containing pigment coatings. Particle size estimates from one pigment manufacturer are given as 0.1 to 1.0 micrometer in diameter, with an average diameter of 1/4 micrometers; another gave nearly all particles under 0.2 micrometers, with about 2% ranging up to 0.40 micrometers.(1)

Estimates of $TiO_2$ content in emissions by source are given in Table XV.(2)

## 3. Potential Environmental Contamination from Package, Transport and Storage

Packaged shipments of titanium dioxide primarily for pigment use are made in paper sacks containing 25 kg. (50-56 pounds). Bulk shipments are made in tank rail cars and tank trucks.(3) Paper mills receive a slurry of anatase in water shipped via tank cars and tank trucks. Paint manufacturers receive shipments of rutile as a slurry.(4)

Titanium dioxide is handled as an inert material. However, damp or wet storage areas may promote the degrading of its physical properties.(5)

## 4. Potential Environmental Contamination from Application and Use

The primary focus for environmental concern when $TiO_2$ is utilized industrially is the aerosol dispersion. Occupational exposures to $TiO_2$ consist

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1. GCA Corporation, *op. cit.*, p. 28
2. *Ibid.*, pp. 10-12
3. *Kirk-Othmer Encyclopedia of Chemical Technology*. *op. cit.*, p. 408
4. Harry Hyman, *loc. cit.*
5. *loc. cit.*

## TABLE X

## SOURCES AND ESTIMATES OF TITANIUM-CONTAINING EMISSIONS

| | Uncontrolled Particulate Emission Factor | | Reliability Code | Production Level (tons/yr) | %$TiO_2$ in Emissions | Reliability Code | $TiO_2$ Emissions Before Coutrols | Estimated Level of Emission Control | $TiO_2$ Emissions After Controls (tons/yr) |
|---|---|---|---|---|---|---|---|---|---|
| | (lb/ton) | (kg/kgx$10^3$) | | | | | | | |
| 1. **MINING & BENEFICIATION** | | | | | | | | | |
| Open Pit Mining | .2 | .1 | (D) | 1,850,000 | 15 | (A) | 30 | 0 | 30 |
| Beneficiation | | | | | | | | | |
| Open Pit | 38 | 19 | (B) | 152,000 | * | (B) | 2,890 | 90% | 289 |
| Dredging | 9.5 | 4.75 | (D) | 308,000 | * | (B) | 1,460 | 90% | 146 |
| 2. **METAL PROCESSING** | | | | | | | | | |
| Metal Ingots | 0 | 0 | | - | - | | 0 | - | 0 |
| Carbides | 0 | 0 | | - | - | | 0 | - | 0 |
| Alloys: | | | | | | | | | |
| Titanium-Base | 0 | 0 | | - | - | | 0 | | 0 |
| Ferrotitanium | 150 | 75 | (D) | 5,872 (tons of alloy) | 45% | (C) | 200 | 40% | 120 |
| Steel Production | 25 | 12.5 | (C) | 2,590 ($TiO_2$ consumed as Ferrotit. in steel mfg.) | * | (-) | 31 | 78% | 7 |
| 3. **OTHER MINERAL USES** | | | | | | | | | |
| Welding Rod Coating | 0 | 0 | (D) | - | - | | 0 | - | 0 |
| Ceramics | 16 | 8 | (C) | 370 | * | | 3 | 67% | 1 |
| Fiberglass | 2 | 1 | (C) | 27,000 | * | | 27 | 0% (controls generally not used) | 27 |
| Pigment Production | | | | | | | | | |
| Sulfate Calcining | 150 | 75 | (B) | 344,000 | 100% | (B) | 25,000 | 97% | 750 |
| Grinding | .35 | .175 | (C) | 655,000 | 100% | (A) | 115 | 10% | 104 |
| Drying & Sacking | NA | NA | | 655,000 | 100% | (A) | NA | 99.5% | 3,275 |
| 4. **PIGMENT CONSUMPTION** | | | | | | | | | |
| Paints, etc. | 15 | 7.5 | (D) | 385,000 | * | | 2,880 | 10% | 2,600 |
| Other Uses | 15 | 7.5 | (D) | 270,000 | * | | 2,020 | 5% | 1,920 |
| 5. **INADVERTENT EMISSIONS** | | | | | | | | | |
| Coal Burning | NA | NA | | 33,800,000 U.E. | 1.2% | (A) | 405,000 | 82% | 73,000 |
| Coal Cleaning | NA | NA | | 2,000,000 U.E. | 0.12% | (A) | 2,400 | 85% | 360 |
| 6. Oil Burning | | | | | | | | | |
| Residual | NA | NA | | 123,000 U.E. | .05% | (A) | 62 | 0 | 62 |
| Distillates | NA | NA | | 146,000 U.E. | .0065% | (B) | 10 | 0 | 10 |
| 7. INCINERATION | NA | NA | | 100,000 U.E. | 4.2% | (B) | 4,200 | 37% | 2,650 |
| 8. Non Metallic Minerals | NA | NA | | 6,900,000 (controlled emissions) | ** | (D) | ** | ** | 3,000 ** |
| U.S. TOTALS | | | | | | | 446,328† | | 88,351 |

NA = Not Applicable

U.E.= Uncontrolled Emission

† Does not include pigment drying and non-metallic minerals

* Emission factor multiplier equal to tons of $TiO_2$ processed or handled annually

** See Text

chiefly of dust and fumes from electric furnace operations.(1) Above the OSHA-established exposure limit of 15 mg/M$^3$, $TiO_2$ dust can cause irritation to those working with it or present in the work areas.

Available information on users of titanium dioxide pigments indicate that occupational exposure may be considerable in some manufacturing processes (e.g., rubber) while it is negligible in others (e.g., hosiery). "This information, however, is fragmentary and should be viewed as such."(2)

## 5. Environmental Contamination Potential from Disposal

Wastes from the sulfate process have long been recognized as one of the major problems facing the industry. Indeed the type and volume of these wastes have made the pollution control problems as significant as any industrial pollution control problem. An example of one such problem involves the dumping of wastes from a new factory for titanium dioxide manufacture at Scarlino in central Italy. Marine scientists raised concerns over the approximately 3,000 tons of waste containing residuals of minerals, sulfuric acid, and small quantities of heavy metals (such as chromium) derived from the ilmenite processing and being dumped daily by small boats just off the shore from the factory. As the factory reaches full operation the amounts dumped will increase. Although laboratories have been gathering data and toxicity studies are in progress, it is not possible to run toxicity tests on all the species in the affected part of the Mediterranean, nor can the long-term influence ever be totally evaluated for all living organisms. The movement of waves, currents and

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1. Frank A. Patty, Editor, Industrial Hygiene and Toxicology, Volume II, Toxicology (New York: Interscience Publishers, 1967) p. 1155

2. W. Kenneth Poole and Donald R. Johnston, Estimating Population Exposure to Selected Metals -- Titanium, Final Report, NIH-ES-2434, PB-195 819 (Springfield, Virginia: NTIS, U.S. Dept. of Commerce, March 1969) p. 48

tides will probably prevent high concentrations occurring in the immediate dumping area for some time, but the dispersion of the so-called red mud ("melma rosa") is considered a "serious blow" to the already precarious life of the Mediterranean.(1)

With the reduction or possible elimination of ocean dumping, the sulfate process has faced increasing pressure on waste disposal. The recovery of ferrous sulfate (copperas) is possible, but the markets for this product are limited especially since it can be produced as a by-product from the sulfuric acid pickling of steel. Although neutralization of waste is possible, the resulting large volumes of hard to dewater solids create a significant solid waste disposal problem. The long-term disposal of those solids into land areas presents potential for hazards due to the leaching of iron and trace metals (such as arsenic, chromium, copper, mercury, lead) into ground or surface waters. Consequently, the pressure on environmentally safer methods of waste disposal accelerated conversion to the chloride process. Although the chloride process should reduce the magnitude and difficulties of waste disposal, land disposal of the remaining solids will remain a problem.

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1. Aristeo Renzoni, "Trouble for the Mediterranean," Marine Pollution Bulletin. 4 (February 1973) p. 19

## D. Current Handling Practices and Control Technology

### 1. Special Handling in Current Use

From an occupational health standpoint, titanium dioxide is considered to be non-toxic, chemically non-irritating, and classified as a nuisance dust. General occupational safety and health recommendations do not stipulate eye protection, protective gloves, or respiratory protection for those using $TiO_2$ under normal handling conditions. However, under certain conditions it is considered an air contaminant, and special handling is required, including protective gloves and glasses. A non-toxic particle mask and ventilation, such as mechanical exhaust, may be desirable under conditions of excessive dusting and/or for clean-up. U.S. Department of Labor's OSHA suggests mine safety appliance #66 CM 73053 type filter.(1) Although considered not injurious, titanium dioxide in contact with the eye should be flushed with water.

A typical Materials Safety Data Sheet for coatings, resins and related materials suggests (per OSHA Standards Section 1910-93 as amended 8-13-71 -- Air Contaminant) a TLV of 15 $mg/m^3$ for titanium dioxide pigment. For respiratory protection, a dust respirator is required when an employee's exposure in any 8-hour work-shift of a 40-hour work week will exceed the OSHA 8-hour time weighted average of 15 milligrams per cubic meter, and the use of a local exhaust fan is recommended.(2)

Because it is non-combustible, $TiO_2$ is not considered a fire and explosion hazard.(3)

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1. E.I. du Pont de Nemours & Co., Pigments Dept., Materials Safety Data Sheets
2. Kerr-McGee Chemical Corp., Materials Safety Data Sheet
3. NL Industries, Titanium Pigment Division, Materials Safety Data Sheet

Being stable, $TiO_2$ is compatible with other materials and does not decompose. It has a specific gravity approximately 4 ± (with $H_2O = 1$) depending on the formulation and its percent volatility by volume is maximum 0.5.(1) General chemical properties of inertness and insolubility may account for general industrial experience where $TiO_2$ has not been associated with organic disease.

## 2. Current Methods for Transport and Storage

Many consumers of titanium dioxide pigments are currently obtaining bulk shipments in two forms: dry bulk and aqueous slurry, as both of these are offered at a lower price than the bagged material. In addition, the consumer realizes savings in labor and economies in elimination of waste and bag disposal.

In dry bulk form, titanium dioxide pigments are considered more versatile than aqueous slurries, which are limited to use in water-based systems. On the other hand, titanium dioxide pigments in aqueous slurry can be used upon receipt without requiring additional dispersion.

In general, storage and handling systems for the aqueous slurry require only relatively standard equipment. However, the dry bulk systems require more sophisticated pneumatic handling techniques due to the fact that $TiO_2$ pigments are not free flowing powders. Live bottom bins, vibration heavy duty rotary powder valves and automatic self-cleaning bag filters are necessary.

In either case, the choice of packaging systems is largely one of economics. It is based generally on minimum yearly consumption of pigment.(2)

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1. E.I. du Pont de Nemours & Co., Pigments Dept., Materials Safety Data Sheets
2. E.I. du Pont de Nemours & Co., Du Pont Ti-Pure® Titanium Dioxide for Plastics. (Wilmington, Delaware: E.I. du Pont de Nemours & Co., 1974) p. 19

Titanium dioxide must be stored in a clean dry area. Protection from water or moisture is necessary to maintain dispersibility. In addition, condensation of water or moisture may degrade physical properties.

## 1. Current Treatment and Disposal Methods

Several treatment and disposal methods for titanium dioxide wastes have been in practice for years, but there are many instances where for a variety of reasons, both environmental and economic, alternatives to current practices are being sought. The factors involved in the choice of alternatives range from stream classification and the assimilative capacities of a given body of water to aesthetic considerations and efforts to improve air and water quality. Whenever possible or feasible, waste products are recycled or recovered as saleable products. Acidic wastes are neutralized before final disposal. An estimate for installation of neutralization treatment and performance is shown in Table XVI.(1)

Conventional waste disposal methods have been ocean dumping, landfill, and, to a lesser extent, deep-well injection. Ocean dumping has been widely used for disposal of iron-acid sludge, while landfill is commonly used for disposal of chloride-process wastes.

### a. Ocean Dumping

Despite its costs, the barging of $TiO_2$ plant wastes to the sea has been in fairly widespread use throughout the industry for many years, where reasonably convenient. The total capital investment costs of initiating a barging operation was $2.1 million, according to one plant manager; of this $1 million was spent to complete on-shore facilities.(2) Costs for barging

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1. U.S. Environmental Protection Agency, Development Document for Effluent Limitations Guidelines...Major Inorganic Products. op. cit., p. 178

2. Samuel W. Fader, "Barging Industrial Liquid Wastes to the Sea," Journal of the Water Pollution Control Federation, 44 (2), (February 1972) p. 316

during the first 8 months of 1971 were approximately \$3,80/1,000 gallon for a 200 nautical mile round trip from the dock. This cost included the operation, maintenance, and depreciation of shore facilities, barge leasing and towing, and dry dock overhaul and repainting of the barge on a 3-year frequency.(1)

The utilization of ocean dumping avoids complicated developmental technology. Barging to the sea has the advantage of reducing waste loads to streams and rivers. Shore facilities supporting this method of disposal include pumps, lines, storage tanks and barge loading equipment, usually gravity fed.

### b. Neutralization and Landfill

In some instances the wastes are collected and concentrated for the removal of solid matter. However, due to the fine particle size, extensive settling time and area are required. The residual solids are neutralized and hauled for sanitary landfill. Due to its inertness, discharge into sewers would impart turbidity which is one of the reasons landfill of this waste is chosen.

### c. Deep-Well Injection

The plant location and the difficulty of finding appropriate deep-well storage capability is central to the question of $TiO_2$ waste disposal by means of deep-well injection. In general, the acid wastes are diluted before discharge into the wells.

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1. Samuel W. Fader, op. cit., p. 318

## TABLE XVI

## INSTALLATION OF NEUTRALIZATION TREATMENT AND PERFORMANCE

| Methods | Estimated Installation Time | Estimated Performance |
|---|---|---|
| Neutralization of acid to $CaSO_4$ and oxidation of iron, and remove for sale or stockpile (as ferrous sulfate) of process wastes and cooling water | 22 mos | Reduce C.O.D. to Nil<br>Reduce acidity to Nil<br>Reduce Fe, Mn, V, and Cr to Nil<br>TDS 50 mg/l |
| Additional settling ponds for cooling waters | 22 mos | Reduction of suspended solids formed due to neutralization by 95% |

### 4. Current Accident Procedures

In the case of $TiO_2$ spillage or leakage, standard protective equipment is required for the clean-up. As described in the first part of this section, respiratory protection of the Mine Safety Appliance #66 CM 73054 Type Filter is required, along with protective gloves, glasses and mechanical ventilation.

### 5. Current Controls

According to the U.S. Food and Drug Administration's regulations, a special grade of $TiO_2$ for use as a color additive in foods, drugs or cosmetics is necessary. The essential requirements involve the control of impurities, including 99.0% $TiO_2$ minimum, 10 ppm acid soluble lead maximum, 1 ppm acid soluble arsenic maximum, 2 ppm acid soluble antimony maximum, 1 ppm acid soluble mercury maximum.(1)

However, there are generally no restrictions on the $TiO_2$ composition for use as a component in food packaging.

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1. "Color Additives" -- Part 8, Title 21, Federal Register, 31 (18), (27 Jan. 1966) pp. 1065

### 6. Control Technology Under Development

Out of the many research and development efforts currently under way to discover new and improved technology for treating and/or disposal of process wastes, some directions for the future of $TiO_2$ control are emerging. For example, American Cyanamid is reported to have investigated neutralization, chemical, catalytic and atmospheric oxidation, acid concentration and recovery, electrodialysis, ion exchange, deep-well injection, and production and sale of a sulfate by-product. A company spokesman, however, has said that none of these methods proved "technologically practical, sound and economically feasible."(1)

On the other hand, Du Pont has spent "well over $1 million" to research alternatives to the treatment and disposal of $TiO_2$ wastes. "Electrolytic oxidation of ferric chloride manufacture for the waste-treatment market" is considered the most promising from this research effort.(2) Du Pont emphasizes that $TiO_2$ waste-treatment and disposal is both an engineering and an economic problem.

Under an EPA grant of $149,000, New Jersey Zinc has been operating a sulfuric acid recovery pilot plant for its $TiO_2$ wastes.(3) The general opinion is that acid recovery is technologically but not economically feasible although New Jersey Zinc has not made full disclosure of its findings.

Another development is related to the fact that Universal Gypsum of Indiana has filed application for patents on their process of making acid wastes into gypsum.(4) It is hoped that the Universal process can be applied to $TiO_2$ wastes in a manner similar to its applications to treat and convert a calcium sulfate waste stream from pharmaceutical plants into pharmaceutical-grade gypsum.

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1. "Heavy Going Ahead for Wastes Discharging at Sea," Chemical Week, 112 (26), (27 June 1973) p. 45
2. Loc. cit.
3. Loc. cit.
4. Ibid., p. 47

## E. Monitoring and Analysis

### 1. Analytical Methods

In general, the analytical methods for wastes from the manufacture of $TiO_2$ vary, depending on the medium, i.e., air, water. From an environmental standpoint analysis is usually performed to determine the presence of total titanium. If titanium is not found, no further tests are performed for titanium dioxide.

#### a. Analysis of Air

Analyses of emissions are generally made for any titanium particulate and not $TiO_2$ *per se*. The primary standard colorimetric method employed for measuring titanium originated with Weller in 1882 and was used further by Lundell and others. It is one in which the yellow complex formed by the addition of hydrogen peroxide to an acid solution of titanium sulfate is measured spectrophotometrically. This method is sensitive with a range of 5 to 50 ppm. In another method, the use of Tiron, an extremely sensitive reagent, imparts a yellow color in the presence of Ti in the 0.3 to 3.0 ppm. range. Another possible method is atomic absorption with optimum concentration in the 5 to 100 ppm range. Both the colorimetric methods and atomic absorption require complete dissolution of the sample, a procedure which can be somewhat tedious. For qualitative purposes, emission spectrography can be used for titanium. X-ray diffraction is used specifically for the crystalline forms of $TiO_2$ and can differentiate between anatase and rutile.

#### b. Analysis of Water

In the analysis of water the solubility of $TiO_2$ is so slight that filtration is usually necessary prior to performing x-ray diffraction. For the same reason, one must filter for the purpose of an x-ray fluorescent scan of a water sample. Once a trace is found, atomic absorption techniques are utilized. The only specifically applicable qualitative measure for $TiO_2$ is x-ray diffraction or electron diffraction performed by an electron microscope. It is particularly important during sampling to determine that the titanium is not from the clay or some other natural and non-polluting source.

In some instances a mobile water testing unit is employed to monitor given sampling sites. Methods may vary from site to site and from parameter to parameter measured, e.g., flow rates may be measured by installed meters, direct collection of small outfall streams, volumetric measurement, dye tracer for velocity measurement, etc.

Tables XVII and XVIII show the analyses of the composition of effluent streams after treatment.(1) The effluent is from a plant utilizing the chloride process. The raw material feed for this plant is over 95% $TiO_2$ grades of rutile and upgraded ilmenite.

## 2. Current Monitoring

There are monitoring programs being employed at $TiO_2$ plants by the manufacturers, as well as those programs concerned with the environment surrounding the facility. At Du Pont, for instance, continuing tests of their products for heavy metals associated with $TiO_2$ manufacture show mercury content in amounts less than 0.1 ppm. This determination of mercury is carried out by an independent laboratory by Multi-Channel Gamma Ray Spectrometry. Based on a doped sample with 1,000 ppb of mercury fixed as HgS, the apparent recovery is 96% and confirms Du Pont's own extraction data.(2)

Waste originating from a NL Industries' $TiO_2$ plant and barged to the N.Y. Bight, off the N.J. coast, has been monitored. The waste consists of 10% ferrous sulfate and 8.5% sulfuric acid dissolved in fresh water. The

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1. U.S. Environmental Protection Agency, Development Document for Effluent Limitations Guidelines...Major Inorganic Products. op. cit., p. 171-2

2. E.I. du Pont de Nemours & Co., Pigments Dept., Materials Safety Data Sheet

## TABLE XVII. COMPOSITION OF PLANT EFFLUENT STREAMS AFTER TREATMENT

| Parameter* | Stream No. 1 | | Stream No. 2 | |
|---|---|---|---|---|
| | Average | Range | Average | Range |
| Suspended Solids | 18 | 1-50 | 15 | 0-40 |
| Total Dissolved Solids | 3300 | 1500-4500 | 300 | 180-900 |
| COD | 50 | 40-90 | 20 | 5-45 |
| pH | 7.8 | 6.0-9.0 | 6.8 | 6.0-9.0 |
| Temperature, °C | 16 | 7-27 | 16 | 2-32<br>(Ambient Temp.) |
| Organics | | None were found | | |
| Turbidity (Jackson Units) | 20 | 10-80 | 20 | 10-50 |
| Color (APHA Units) | 10 | 10-20 | 10 | 10-20 |
| Chloride | 1650 | 750-2050 | 50 | 70-100 |
| Sulfate | -- | 1-2.5 | -- | 1-2.5 |
| Sulfate | -- | -- | 150 | 90-450 |
| Iron | 0.2 | 0-3.0 | 0.2 | 0.1-1.0 |
| Copper | 0.015 | 0.01-0.03 | 0.015 | 0.01-0.03 |
| Chromate | 0.01 | | 0.01 | |
| Total Chromium | 0.05 | 0.01-0.15 | 0.05 | 0.01-0.15 |
| Arsenic | 0.02 | | 0.02 | |
| Mercury | 0.001 | | 0.001 | |
| Lead | 0.14 | 0.1-0.19 | 0.02 | 0.02 |

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*mg/l unless otherwise specified

## TABLE XVIII. VERIFICATION DATA FOR THE PLANT

| Parameter* | | Lake Intake Water | Effluent Stream #1 | Effluent Stream #2 |
|---|---|---|---|---|
| Flow, cu m/day (MGD) | | 3650 (0.964) | 6060 (1.60) | 2240 (0.590) |
| Temperature, °C | | 9 | 16 | 26.5 |
| Color (APHA Units) | | 100 | 140 | 90 |
| Turbidity (FTU) | | 35 | 35 | 30 |
| Conductivity | | 100 (NaCl) | 2100 (NaCl) | 170 (NaCl) |
| Suspended Solids | | 25.0 | 10 | 30 |
| pH | | 7.9 | 7.6 | 6.85 |
| Acidity: Total | | N/A | N/A | 0 ($CaCO_3$) |
| Free | | N/A | N/A | 0 ($CaCO_3$) |
| Alkalinity (Total) | P | 0 ($CaCO_3$) | 0 ($CaCO_3$) | 0 ($CaCO_3$) |
| | T | 93 ($CaCO_3$) | 22 ($CaCO_3$) | 28 ($CaCO_3$) |
| Hardness: Total | | 129 ($CaCO_3$) | 2600 ($CaCO_3$) | 185 ($CaCO_3$) |
| Calcium | | 97 ($CaCO_3$) | 1920 ($CaCO_3$) | 139 ($CaCO_3$) |
| Halogens: Chlorine | | 0 | 0 | 0 |
| Chloride | | 36.5 | 2250 | 49.5 |
| Fluoride | | 0 | 0.3 | 0.25 |
| Sulfate | | 32.0 | 240 | 175 |
| Phosphates (Total) | | 1.4 | 0.025 | 0.225 |
| Nitrogen (Total) | | 0.24 | 0.14 | 1.3 |
| Heavy Metals: | | | | |
| Iron | | 0.225 | 1.6 | 0.4 |
| Chromate | | 0 ($Cr^{+6}$) | 0 ($Cr^{+6}$) | 0 ($Cr^{+6}$) |
| Oxygen (Dissolved) | | 10.8 | 9.0 | 6.2 |

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*mg/l unless otherwise specified

turbulent wake of the barge dilutes and neutralizes the discharge rapidly, so that the acidification of the sea water is short lived. Turbidity of the water results, however, from the formation of ferrous hydroxide.(1)

In a federal government support grant, The Marine Laboratories of the University of Delaware developed a biological and bottom-monitoring program for the disposal area associated with the nearby $TiO_2$ pigment plants. Conclusions from this study showed (a) "no change in ocean quality or accumulation of waste materials in the disposal area" with wastes being transported to sea by normal ocean currents; (b) relatively rapid (10 to 20 minutes) initial dispersion of wastes behind the barge, about 1 to 5,000-fold dilution; (c) the marked influence of a "thermocline" on the vertical dispersion or mixing of the wastes, resulting in protection of marine life on the ocean bottom from contact with the dispersing wastes during the warm seasons but not the cold; (d) a mathematical model simulating the dispersion pattern observed; (e) no changes in the marine life of the water column attributable to the disposal operation with the possible exception of the sand dollar.(2)

Although the evidence in relation to possible effects on the sand dollar was inconclusive, the sand dollar is considered important in the general ecology of the sea. The sand dollar, *Meoma ventricosa*, also called the cake dollar, is an irregular echinoid identified as one of the 6,000 existing species of echinoderms. Echinoderms are marine invertebrates that are important to the general ecology of the sea, serving as scavengers of decaying matter on the sea floor and consumers of various organisms.

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1. Jelks Barksdale, Titanium, Its Occurrence, Chemistry and Technology, (New York: Ronald Press Co., 1966, Second Edition) p. 370

2. Samuel W. Fader, op. cit., pp. 317-18

Du Pont's technical manager of plants, Hal Clark, has been quoted as saying that the typical waste stream in 100 lbs. of $TiO_2$ production from the sulfate process contains:(1)

| | | |
|---|---|---|
| | 220 lbs. | sulfuric acid |
| | 150 lbs. | ferric sulfate |
| | 15 lbs. | other sulfates |
| | 6 lbs. | neutral salts |
| Total | 391 lbs. | waste |

and from the chloride process contains:

| | | |
|---|---|---|
| | 18 lbs. | hydrochloric acid |
| | 85 lbs. | ferric chloride |
| | 10 lbs. | other chlorides |
| | 6 lbs. | neutral salts |
| Total | 119 lbs. | waste |

Another example of a monitoring program is one being carried out in the German Bight in connection with the $TiO_2$ factory near Bremerhaven. The pH in the samples is measured by a glass electrode, Fe concentration is determined by gravimetry and photometry and the $O_2$ concentration by titration. The most important changes noted in this case include a reduction in the pH of the sea water from 8.1 to 8.2 and marked increase in the $CO_2$ partial pressure. In addition, the ferrous sulfate increases the iron concentration, and the $Fe^{2+}$ is oxidized to $Fe^{3+}$ and precipitated as hydroxide, resulting in an $O_2$ deficit in the sea water.(2)

Tests were made to determine the penetration of the wastes (with a density of 1.25 g/$cm^3$) to the sea bed. Contrary to expectations, the wastes did not reach the sea bed during the first hours after release. The pH and

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1. "Heavy Going-Ahead for Waste Discharging at Sea," op. cit., p. 47
2. G. Weichart, "Chemical and Physical Investigations on Marine Pollution by Wastes of a Titanium Dioxide Factory," Marine Pollution and Sea Life. Mario Ruivo, General Editor (London: Fishing News Ltd., 1972) pp 186-8

$O_2$ content returned to about normal but the Fe concentration in the bottom layer increased shortly after release. After five and a half months, the highest Fe concentration in the sea water 5 m below the surface was 0.5 mg/l, and there was no change in pH. Although ferric hydroxide, formed by reaction of the wastes with sea water, sank to the sea bed, it was determined after 5 1/2 and 16 months that the Fe content in the upper layers of the sediment was no greater than that measured before the disposal of waste.(1)

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1. G. Weichart, loc. cit.

## III. HEALTH AND ENVIRONMENTAL EFFECTS

### A. Environmental Effects

#### 1. Persistence

As mentioned in previous sections, titanium dioxide is insoluble in water, HCl, $HNO_3$ or dilute $H_2SO_4$.(1) The suggested waste disposal method has been sanitary landfill. Under these conditions, the compound would be expected to be very persistent. No information appeared in the literature reviewed concerning biological degradation, and chemical degradation seems unlikely under normal circumstances.

#### 2. Environmental Transport

No information was found concerning environmental transport of $TiO_2$. However, movement would be expected as with any inert particulate.

#### 3. Bioaccumulation

Concentration of titanium in plants is extremely variable. Green portions of plants generally contain more than roots or stems. There is no evidence that plants preferentially accumulate the element, nor are there data available as to the form of titanium taken up by plants.(2) Schroeder et al mention that A.P. Vinogradov at the Sears Foundation for Marine Research, Yale University, reported in a study of the elementary composition of marine organisms, published in 1953, that titanium can be absorbed and concentrated by factors of 4 to 180 by algae, plankton, protozoa, sponges, corals, starfish and crustaceans. Fish, however, absorb and store it poorly.(3)

Samplings of wild animal tissues suggest that titanium is not accumulated to any degree. The wild animals (woodchuck, muskrat, red squirrel, red fox, deer, etc.) were from Southern Vermont. For the woodchuck, concentrations (wet wt) of titanium were reported as 0.0 or 0.32 μg/g in the

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1. The Merck Index. op. cit., p. 1054
2. H.A. Schroeder, J.J. Balassa, and I.H. Tipton, "Abnormal Trace Metals in Man: Titanium," Journal of Chronic Diseases, 16 (1963) pp 55-69
3. Ibid., p. 63

kidney, and as 0.53, 1.00, and 1.50 μg/g in the spleen. For the deer, concentrations in the kidney ranged from 0.31 to 3.10 μg/g.(1)

Studies in laboratory animals (mice) given soluble salts of titanium showed that considerable quantities were accumulated, as much as 32.49 μg/g being found in albino mice.(2)

Despite this large accumulation, continuing investigation showed no evidence of toxicity of titanium for mice. There was no increase in mortality during 18 months in mice given the metal, and mature weights of the animals were significantly greater than those of the controls.(3)

The available literature, therefore, suggests that the form, e.g., solubility, of titanium is a major determining factor in its bioaccumulation. Titanium dioxide which is insoluble would be expected to be taken up and accumulated to a lesser extent than soluble salts.

### 4. Biomagnification

There were no data available concerning biomagnification.

## B. Biology

### 1. and 2. Absorption and Excretion

There is no apparent evidence that titanium dioxide is absorbed from the gastrointestinal tract following oral administration in animals. In a study to test the value of titanium dioxide as an index material for determining apparent digestibility of a rat diet, thirty male albino rats, averaging 60 days of age, were fed a diet containing 0.25% $TiO_2$ for a 13-day period. The diet consisted of 90% ground wheat plus 10% of a protein-mineral supplement. Total feces from these animals were collected individually and daily for 13 days or were pooled for groups of

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1. W.A. Schroeder, J.J. Balassa, and I.H. Tipton, *op. cit.*, p. 61
2. *loc. cit.*
3. *Ibid.*, p. 67

five animals each for a period of seven days from days 6-13. All feces samples were analyzed for $TiO_2$ by a colorimetric method (modification of Weller's Method). For all treated animals, the average recovery of titanium dioxide over the 7-day period from days 6-13 was 92.0%. The rate of excretion was somewhat delayed since analyses of daily samples of feces for the first six days showed that a constant and maximum excretion of $TiO_2$ had not been attained. The authors concluded that it was unlikely that $TiO_2$ was absorbed from the gastrointestinal tract, since, with progressing time, the average digestion coefficients approach the values determined conventionally. The delayed excretion of $TiO_2$ appeared to be due to its accumulation in some part of the tract, possibly the cecum.(1)

Another study investigated the passage of titanium dioxide through the gastrointestinal tract.(2) Rats were administered diets containing 0.42 gm calcium carbonate together with 0.2, 1.0 and 2.0 gm titanium dioxide/100 gm diet for seven days. At sacrifice, the ratios of the amounts of calcium to titanium dioxide at various points along the length of the gastrointestinal tract in these animals were not found to differ appreciably from that present in the diet. This finding supports the view that titanium dioxide is not absorbed. In addition, the blood, liver, kidneys or urine of rats which had ingested 0.66 gm $TiO_2$/kg body weight daily for 15 days contained no amounts of titanium that were detectable by an assay sensitive to 10 µg.(3)

The absorption of titanium from the gastrointestinal tract may be dependent upon the solubility of the salt employed. A study was made in which albino mice administered a soluble titanium salt, potassium titanium oxylate, at a dosage level of 5 ppm in drinking water from weaning throughout life span, showed greater Ti concentrations in the lungs, spleen, kidneys, and liver

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1. L.E. Lloyd, Elaine Rutherford, E.W. Crampton, "A Comparison of Titanic Oxide and Chromic Oxide as Index Materials for Determining Apparent Digestibility," Journal of Nutrition, 56 (1955) p. 265-71

2. P. Fournier, De l'Emploi de l'Oxyde de Titane Pour l'Etude Quantitative de l'Absorption Intestinale, Comptes Rendus des Seances de l'Academie des Sciences, 231 (1950) p. 1343-5

3. loc. cit.

than did control animals. These concentrations did not, apparently, affect the mortality of the males and, as mentioned earlier (p.58), showed no evidence of toxicity to the mice. Maximum precautions were taken in this experiment against introducing titanium contamination from outside sources.(1)

In rats, deposition of titanium dioxide has been demonstrated in the lungs and lymph nodes following inhalation and intratracheal injection.(2, 3, 4) Qualitative and quantitative analyses of lung tissue of three workers employed in a titanium dioxide processing factory in Finland also showed considerable titanium content.(5) The results of these studies are presented in detail below and on pp. 70-1.

When $TiO_2$ was used as a protective film on exposed parts of the body for the prevention of flash burns during World War II, no adverse reactions followed, indicating that it did not have the capacity to produce contact dermatitis, allergic sensitization, or appreciable dermal absorption.(6)

### 3. Transport and Distribution in Living Organisms

In a series of experiments, the rate of removal of titanium dioxide from blood and its deposition in liver, spleen and celiac lymph nodes was studied

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1. H.A. Schroeder, W.H. Vinton, Jr. and J.J. Balassa, "Effect of Chromium, Cadmium and Other Trace Metals on the Growth and Survival of Mice," Journal of Nutrition, 80 (1963) p. 39-47
2. H. Christie, R.J. MacKay and A.M. Fisher, "Pulmonary Effects of Inhalation of Titanium Dioxide by Rats," American Industrial Hygiene Association Journal, 24 (1), (1963) p. 42-6
3. J. Ferin, "Papain-Induced Emphysema and the Elimination of $TiO_2$ Particulates from the Lungs," American Industrial Hygiene Association Journal 32 (1971) p. 157-62
4. C.J. Göthe and A. Swensson, "Effect of BCG on Lymphatic Lung Clearance of Dusts with Different Fibrogenicity. An Experimental Study in Rats," Archives of Environmental Health, 20 (1970) p. 579-85
5. R.K. Elo, K. Maata, E. Uksila and A. Arstila, "Pulmonary Deposits of Titanium Dioxide in Man," Arch. Path., 94 (4), (1972) p. 417-24
6. Frank A. Patty, Editor, op. cit., p. 1157

in rats following a single intravenous injection. In each study female Sprague-Dawley rats 45-55 days of age and 145-155 gm in body weight were used. The sample of $TiO_2$, which had an anatase crystal structure and was water-dispersible, was 99% pure with a lead content of 0.0016%. The particle size was 0.2-0.4 microns. Dosages of $TiO_2$ were prepared as suspensions in 5% dextrose (2.5 gm/100 ml) and injected intravenously into the caudal vein. $TiO_2$ tissue content was determined by a modification of the technique of Hillebrand and Lundell, the limit of sensitivity of which was about 1 μg/ml.(1)

A single rat was injected intravenously with 250 mg $TiO_2$/kg body weight and blood samples taken at 5-minute intervals for $TiO_2$ determination. The removal of $TiO_2$ from the blood was found to occur at an exponential rate with whole blood concentrations at +5, +10, and +30 minutes determined as about 290, 90 and 25 μg $TiO_2$/cc, respectively.

In another series of experiments, eight rats/group received a single intravenous injection of 250 mg $TiO_2$/kg body weight. Animals were killed at 0, 6, 12 and 24-hr intervals for determination of $TiO_2$ content in the liver, spleen and celiac lymph nodes. Another animal was killed one year after injection. In those rats killed immediately following injection, 69 and 78% of the injected dose was found in the liver at 5 and 15 minutes, respectively. Concentrations of $TiO_2$ in the liver, spleen and celiac lymph nodes of animals killed at 6 and 24 hrs, and 1 year are shown in Table XIX.(2) In the 6-hour group highest concentration of $TiO_2$ was found in the liver, and the next highest in the spleen. Titanium was not concentrated in any of the lymph nodes of the celiac group until 12 hours following injection, when the average $TiO_2$ content was determined as 1.2 mg/gm. In contrast, the iliac

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1. C.B. Huggins and J.P. Froelich, "High Concentration of Injected Titanium Dioxide in Abnormal Lymph Nodes," Journal of Experimental Medicine, 124 (6), (1966) p. 1099-1106

2. Ibid., p. 1102

lymph nodes of the same animals contained 0.43 mg $TiO_2$/gm. In the 24-hr group, the relative $TiO_2$ concentrations in the three tissues were as follows: "white celiacs" (those celiac lymph nodes with grossly-apparent high concentrations of $TiO_2$) > liver > spleen.

In the single rat killed one year following titanium dioxide administration, the highest $TiO_2$ concentration was found in the celiac lymph nodes, the titanium content of which exceeded that of the mediastinal lymph nodes by 18 times. Decreasing $TiO_2$ concentrations were found in the mediastinal lymph nodes, spleen and liver. Microscopic examination of the celiac lymph nodes, which grossly did not appear enlarged, showed that the largest amount of titanium dioxide was localized in the medulla.

In another series of experiments, the effect of splenectomy or partial hepatectomy on celiac lymph node $TiO_2$ content was examined. A $TiO_2$ suspension at the dosage level of 250 mg/kg was injected intravenously into rats 24 hours following splenectomy or partial hepatectomy. Control rats did not undergo surgical procedures. Tissues from all animals were collected 24 hours following injection.

## TABLE XIX

## CONCENTRATION OF TITANIUM DIOXIDE IN LIVER, SPLEEN, AND LYMPH NODES

A Single intravenous injection of $TiO_2$, 250 mg/kg, was given at 0 hr to female rats age 45 to 50 days. There were 8 animals in each group.

| Time of harvest | Liver | Spleen | Lymph nodes | |
|---|---|---|---|---|
| | | | Celiac white | Celiac nonwhite |
| | | $TiO_2$:mg/g | | |
| 6 hr. | 4.13 ± 0.4 | 3.0 ± 0.8 | 0.46 | 0.52 |
| 24 hr. | 3.93 ± 0.3 | 1.5 ± 0.4 | 9.1 ± 1.3 | 0.28 |
| 1 yr. | 3.90 ± 0.6 | 18.2 ± 4 | 127.0 | 0.70 |

±, standard deviation

The concentration of $TiO_2$ in the liver of splenectomized rats, injected 1 to 21 days after removal of the spleen, was similar to that of normal controls. Excision of the median and left lateral hepatic lobes, however, had profound effects on the distribution of injected $TiO_2$ which were first apparent 24 hours after surgery. The regenerating liver appeared intensely white at 24 hours after surgery. As in the intact normal control, 80% of the dose of $TiO_2$ was found in the regenerating hepatic lobes despite the fact that the total amount of liver tissue was less than in the normal controls. The number of "white celiacs" was reduced to two compared to 5-7 in control animals; these nodes were located only on the right side of the abdomen around the epiploic foramen. There were no "white celiacs" on the left side of the retroperitoneal space until day 7 after hepatectomy. On day 21, the number and site of white celiac lymph nodes was similar to that of the controls.

The authors concluded that the great accumulation of titanium dioxide in the celiac nodes is attributed to their topography which results in progressive filtration of particulate matter from hepatic lymph rather than any unusual chemical characteristics.(1)

Deposition and clearance of titanium dioxide from the lungs of rats following exposure by inhalation has been studied.(2 and 3). In the former study 22 male Wistar rats, 245-360 gm in body weight, were exposed to $TiO_2$ dust generated four times daily at 2-hour intervals five days/week for 10-13 months by evaporation of an aqueous suspension of $TiO_2$. Dust counts were in the range of 42-328 mppcf (million particles/cubic foot) during the first hour

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1. C.B. Huggins and J.P. Froehlich, op. cit., p. 1105
2. H. Christie, R.J. MacKay and A.M. Fisher, loc. cit.
3. J. Ferin, loc. cit.

and 10-46 mppcf during the second hour. No particle size was given. A comparable group of 23 rats served as controls.

No significant difference was observed between the wet weight of pairs of lungs from treated and control animals after 9-13 exposure months, although the lung ash content of the experimental group was substantially greater than that of the control. Qualitative spectrographic analysis of pooled lung ash from treated rats showed greater than 10% titanium content.

Microscopic examination of the lungs showed aggregates of pigment in the sump areas in the subpleural areas and in the regions of the alveolar ducts after 9-13 exposure months. The pigment occurred intracellularly within the macrophages and was associated with focal areas of emphysema. The alveoli were for the most part free of pigmentation, although small aggregates of macrophages containing pigments were apparent in the bronchial lymph nodes at 13 months. No enlargement of the mediastinal lymph nodes was noted. The appearance of the lungs of rats exposed to dust for 10 months and then to fresh air for three months was identical with that of animals exposed for 13 months. This finding suggests that the clearance of titanium dioxide is delayed.(1)

In the latter study, 10 male Long-Evans rats, about 200 gm in body weight, per group were exposed to concentrations of 7.5 to 50 mg/m$^3$ of anhydrous $TiO_2$ by inhalation for periods of minutes to 7 hours.(2) Prior to exposure, experimental emphysema was produced in two groups of animals by intratracheal injection of 0.5 mg papain (two injections in 4 days) or by papain aerosol (total exposure time 64 hours over two weeks and 48 hours over two weeks). The median mass aerodynamic diameter of the particles was

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1. H. Christie, R.J. MacKay and A.M. Fisher, loc. cit.
2. J. Ferin, loc. cit.

1.48 µm (mean geometric standard deviation of 3.26); the mean specific surface area was 6.5 $m^3$/gm; and in vitro solubility was about $10^{-10}$ gm/$cm^2$/day. Pulmonary $TiO_2$ retention was determined 25 days after exposure by a photometric method using 4,4-diantipyrylmethane monohydrate.

The production of different lung burdens and the use of different exposure time intervals permitted an evaluation of different clearance rates and their relation to the localization of $TiO_2$ particles in the lung tissues. In rats without experimental emphysema, the results showed (1) a direct relationship between $TiO_2$ concentrations following a 7-hour exposure and absolute $TiO_2$ deposition in the lungs, (2) a direct relationship between exposure time and at a concentration of 54 mg $TiO_2/m^3$ and absolute $TiO_2$ deposition in the lungs, and (3) a direct relationship between the lung weight of five different species, including mouse, hamster, rat, guinea pig and rabbit, following a 7-hour exposure to 15 mg $TiO_2/m^3$ and absolute $TiO_2$ deposition in the lung.

The retention of $TiO_2$ in the lung was studied for up to approximately 140 days postexposure. The biphasic retention half-times in three experiments with average initial lung burdens of 60, 139 and 247 µg $TiO_2$ were about the same, "with 14 days applying to the first 8 days, and 88 days, thereafter." The first phase of clearance included mainly, but not exclusively, the particles deposited in the ciliated airways. After 30 minutes of exposure, phagocytosed $TiO_2$ particles were apparent not only within the alveoli, but also within macrophages on the ciliary "escalator."(1)

In rats with papain-induced emphysema, a significant decrease in $TiO_2$ clearance rates was apparent 25 days after exposure as shown in Table XX.

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(1) J. Ferin, op. cit., pp 160-1

## TABLE XX(1)

## TWENTY-FIVE-DAY RETENTION OF $TiO_2$ IN PAPAIN-TREATED RATS

| Experiment | Treatment | Initial Lung Burden ( g/lung) | Retention (%) | P < |
|---|---|---|---|---|
| 1 | Control | 376 | 49 ± 11 | 0.05 |
| | Papain aerosol | 438 | 61 ± 9 | |
| 2 | Control | 326 | 49 ± 7 | 0.01 |
| | Papain aerosol | 293 | 66 ± 13 | |
| 3 | Control | 326 | 49 ± 13 | 0.001 |
| | Papain, intratracheal | 164 | 82 ± 12 | |

In another study, treatment with BCG was also found to increase the retention of $TiO_2$ in the lungs of rats following administration by intratracheal injection. Fifteen female Sprague-Dawley rats, 200 gm in initial body weight, were injected intratracheally with 1 ml of a $TiO_2$ suspension in saline (20 mg/ml). The mean diameter of the particles was 0.6 μ. An intravenous injection of BCG (Gothenburg substrain), a cow-virulent strain of bovine tubercle bacilli, preceded the intratracheal injections of dust by two months. The substrain was supplied as a suspension with a concentration of 20 mg bacilli/ml. Each BCG-treated rat received 5 mg BCG (1 mg contained about $3 \times 10^7$ "viable units"). The animals were sacrificed 60 days after the dust injection. At autopsy, the $TiO_2$ content of the lymph nodes was determined spectrophotometrically while that of the lungs was determined by spectralanalysis.(2)

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1. J. Ferin, *op. cit.*, p. 158
2. C.J. Göthe and A. Swensson, *loc. cit.*

Intratracheal injection of the dust increased both the absolute and relative lung weights, although the reaction was less pronounced than that observed following injection with silica-containing dust. The reaction from $TiO_2$ in the hilar lymph nodes showed the same tendency as in the lungs.

The $TiO_2$ content of the lungs was significantly higher in animals treated with BCG and dust than in corresponding groups treated with $TiO_2$ alone. The tendency was quite the opposite in the hilar lymph nodes where the $TiO_2$ content was significantly higher in the dust-treated control groups than in corresponding experimental groups treated with both BCG and $TiO_2$. These results implied that significant amounts of inert dusts were transported from the lungs through the pulmonary lymphatics and that this transport was retarded by BCG. Formerly, inert dusts had been considered to be mainly eliminated via the bronchi.(1)

In guinea pigs and rabbits, intravenous or intra-tonsillar injection of titanium dioxide has resulted in translocation of the particles to tissues damaged by prior injection of cell-wall components of *Streptococcus*,(2) or tissue-damaging factor protein isolated from extracellular products of group A streptococci or BCG.(3) The results of the latter study indicated that $TiO_2$ particles injected intraperitoneally in rabbits became localized within phagocytic cells in myocardial, hepatic and diaphragmatic lesions induced by streptococcal toxin. It was also

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1. C.J. Göthe and A. Swensson, *loc. cit.*

2. I. Ginsburg and R. Trost, "Localization of Group A Streptococci and Particles of Titanium Dioxide in Arthritic Lesions in Rabbits," *Journal of Infectious Diseases*, *123* (3), (1971) p. 292-96

3. I. Ginsburg, H.A. Gallis, R.M. Cole, and I. Green, "Group A Streptococci: Localization in Rabbits and Guinea Pigs Following Tissue Injury," *Science*, *166* (1969) p. 1161-3

shown that both streptococci and $TiO_2$ particles were localized in delayed hypersensitivity lesions induced in the skin of guinea pigs by injections of tuberculin. It was suggested that the extent of localization of particles in tissues depended upon the severity of the inflammatory process.(1)

## 4. Metabolic Effects

No data concerning metabolic effects of titanium were reported in the literature reviewed.

## 5. Pharmacology

In other studies, an effect of titanium dioxide was observed on the level of circulating thrombocytes following intravenous injection in rats.(2) Anesthesized albino rats, about 300 gm in average body weight, received a single intravenous injection of 1, 2 or 4 mg $TiO_2$ suspended in saline. The particles of $TiO_2$ were characterized as angular and had an average size of 60 mμ. Blood samples were taken at 2, 4, 8, 16 and 32-minute intervals up to 1 hour after injection. Control animals were treated in a similar manner and injected with saline.

Doses of 1 and 2 mg $TiO_2$ produced no appreciable change in thrombocyte count. A dose of 4 mg, however, was followed by a marked decrease in platelet count which was first apparent 4 minutes after injection. This effect lasted longer than 32 minutes. In comparison, injection of 1 mg of amorphous synthetic silica (150 mμ) in suspension also produced a rapid fall in the number of circulating thrombocytes. Maximum reduction was achieved after 4 minutes. Similar results were obtained with a water-soluble starch, but not with colloidal solutions of an iron preparation, methylene blue or saline.

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1. I. Ginsburg and R. Trost, loc. cit.
2. G. Bloom and A. Swensson, "The Reaction of Thrombocytes to Intravenously Injected Suspensions of Submicroscopic Particles," Acta Med. Scand., 162 (1958) p. 423-6

## 6. Tissue Reaction

Compatibility of titanium with soft tissues and bones has been demonstrated histologically following surgical implantation in dogs.(1 and 2) In one of the two studies, small discs of titanium (0.25 in. in diameter and 0.013 in. in thickness) were embedded into the rectus abdominus muscle, left side, of dogs under surgical asepsis. Controls of tantalum (0.25 x 0.010 in.), a proven inert metal, were allowed to remain *in situ* for a period of 7 months. The discs, with an adequate amount of surrounding tissue, were then surgically removed and fixed for microscopic examination.(3)

The gross specimens of titanium and tantalum gave no indication of irritation, infection or inflammation. A fibrous capsule encased the metal in each instance. The microscopic sections confirmed a negative inflammatory and infectious response to both metals, but a fibroblastic response was present. The tissue tolerance response appeared similar. The authors concluded that titanium was well tolerated by living tissue of dogs.

In the second of the two studies, screws and plates (total of 11 plates and 42 screws) of cast Vitallium, wrought Vitallium and Austanium, a trademark for a titanium alloy, were surgically implanted in the body of the mandible and the front and hind legs of anesthesized dogs. The plates were placed over the cortical layer of bone, the screws inserted and the periosteum sutured over both screws and plate. All animals were sacrificed after a period of 2-17 months and were perfused with a 10% formalin solution. Samples of tissue were taken for histological examination.(4)

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1. O.E. Beder and G. Eade, "An Investigation of Tissue Tolerance to Titanium Metal Implants in Dogs," *Surgery*, *39* (1956) p. 470-3

2. P.P. Gross and L. Gold, "Compatibility of Vitallium and Austanium in Completely Buried Implants in Dogs," *Oral Surgery*, *10* (1957) p. 769-80

3. O.E. Beder and G. Eade, *loc. cit.*

4. P.P. Gross and L. Gold, *loc. cit.*

Since no gross or histological differences were noted between the metals or the length of time the metals were implanted, the findings were reported as a composite. Only slight evidence of inflammatory reaction was apparent histologically and was considered negligible. There was no acute or chronic cellular or exudative response. Plasma cells or cells similar in appearance to plasma cells were observed; these were possibly normal hematopoietic elements or even osteoblasts. There was no evidence of either osteoblastic or osteoclastic changes or periosteal proliferation. There was no fibrous tissue barrier present in the long bones between the screw and the bone at any point of contact along the metal path, except where the screws penetrated the inner cortex and the periosteum into the muscle tissue. In contrast, a fibrous capsule was present between the apex of the screw and the medullary space of the mandible.

The authors concluded the cast and wrought Vitallium and Austanium plates and screws, combined or separate, were compatible with soft tissues and the bone, and did not cause any observable clinical or histologic injury.(1)

## C. Toxicity - Humans

### 1. Occupational Studies

Industrial exposure to dust of titanium and titanium dioxide has not been linked with an unusual incidence of illness among workers and hence has not received as extensive investigation as some other industrial compounds. In Finland, lung samples from three men who had worked in a titanium dioxide processing factory for 9-10 years, were examined with light and electron microscopy.(2) All three had displayed pulmonary symptoms including dyspnea, productive cough and recurrent bronchitis which were associated

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1. P.P. Gross and L. Gold, loc. cit.
2. R.K. Elo, K. Maata, E. Uksila and A. Arstila, loc. cit.

with their work. Radiologically, two of the patients showed changes of pneumoconiosis. At thoracotomy, pleural and diaphramic adhesions were found in one of the patients and both had green-colored patches on the lung surface associated with carbon pigment. At autopsy (following unrelated drowning) the third worker also had green-colored patches of pleural changes. Examination with light microscopy showed carbon-like, but birefractive pigment aggregations; the nature of the pigment was not determined. Two of the lungs showed some bronchiolar hyperplastic changes and one emphysema and chronic bronchitis. Electron microscopy revealed numerous phagocytizing cells in the alveolar lumen; the cytoplasm of these cells was filled with electron-dense, single membrane-limited lysosomes which contained numerous black particles. X-ray fluorescence analysis indicated considerable amounts of titanium were present in all three lungs. In two of the cases this was confirmed by optic emission spectrographic analysis. Slight elevations of magnesium, aluminum and silica were seen in two of the lungs; the third had a high concentration of nickel.

In contrast to the above study a study of 136 workers engaged in loading or in extracting ilmenite failed to reveal any such possible effects.(1) The workers were submitted to 70 mm radiography of the chest, clinical examination and interview about respiratory symptoms. Length of service ranged from 1 to 12 years and averaged 4.4 years for all workers, 3.3 years among the most exposed workers. Radiological lesions were observed in three workers of whom only one had a high degree of exposure. All three were asymptomatic. A similar incidence was found among controls. Six workers had respiratory symptoms since starting work at the factory, but none had

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1. C.G. Uragoda and U.R.M. Pinto, "An Investigation into the Health of Workers in an Ilmenite Extracting Plant," Medical Journal of Australia, 1 (4), (1972) p. 167-9

any abnormal physical signs or radiological lesions in the chest. The symptoms were considered to be due to dust per se and not a specific response to minerals.

In response to a request from an employee representative, the National Institute for Occupational Safety and Health of the U.S. Department of Health, Education and Welfare conducted a health hazard survey at the Titanium Pigment Division of the NL Industries, Ltd.(1) Among 15 randomly-selected individuals who were interviewed, none had health complaints or knew of anyone working in his area who had. Nine individuals who had reported health complaints were interviewed. None of these suggested a relationship to exposure to titanium dioxide although several indicated effects (irritant contact dermatitis, plus one case of upper tract and eye irritation) from exposure to monoisopropanolamine (MIPA). Until early 1973, MIPA had been metered into the grinding mills in small quantities to reduce any caking tendency and to insure a final $TiO_2$ product ground to exact specification. Triethanolamine (TEA) was then substituted for MIPA, but was later eliminated prior to 31 May 1973. After the discontinuation of MIPA, no new cases of irritation or dermatitis occurred.

Although monoisopropanolamine and its vapor are not regarded as toxic in the usual industrial setting, MIPA on contact with the skin can cause local effects up to a burn, depending on exposure. It is not, however, considered to be a problem because of this and it is generally considered low in toxicity by this route. Any vapor generated by MIPA should be avoided. Similarly, a single short exposure to TEA can result in mild skin irritation; prolonged or repeated exposure can provoke moderate irritation or even a mild burn. However, TEA is not likely to be absorbed in toxic amounts by the skin. In contact with the eye, MIPA can cause local

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1. R.L. Hervin and J.B. Lucas, Health Hazard Evaluation/Toxicity Determination, NL Industries. NIOSH-TR-068-74, PB-229 604 (Springfield, Virginia: NTIS, September 1973)

effects up to a burn; TEA can cause moderate irritation and corneal injury.

The NL employees were exposed to MIPA (or to $TiO_2$ semi-saturated with MIPA) during maintenance operations or when a leak occurred in the system. The wearing of appropriate protective clothing by employees is recommended, if either MIPA or TEA is reintroduced into the workplace.

The plant appeared to be rather dusty, but respirable levels of titanium dioxide were below the standard permitted. It was concluded that no safety recommendations need be made at the plant although the general housekeeping could be improved to reduce the dust levels. Although there was no evidence of actual or potential pulmonary or other hazard to employees from the $TiO_2$ dust, respirators should be provided and used by the employees, whenever airborne inert or nuisance dust is present in excessive amounts.(1)

## 2. Epidemiology

No epidemiological studies were available for review. Titanium and its compounds have been used in therapy of skin disorders and in surgical appliances over the years with no reports of toxicity from such use.(2)

## 3. Other Controlled Studies

There is very little data concerning controlled studies of the toxicity to humans of titanium dioxide. In 1955, it was reported that the use of

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1. R.L. Hervin and J.B. Lucas, loc. cit.

2. E. Browning, Toxicity of Industrial Metals, Second Edition (New York: Appleton-Century-Crofts, (1969) p. 331-5

titanium salts in ointment and powder preparations over a 3-year period in some one hundred cases had shown therapeutic promise with no toxic effects. However, details are lacking as to how well controlled these studies were.(1)

Preliminary results of efficacy of various agents for protection of the skin from exposure to light suggest that titanium dioxide is an effective agent.(2)

## D. Toxicity - Birds and Mammals

### 1. Acute

The study of Göthe and Swensson, which was discussed in detail (pp.67-8) showed that rats receiving a single intratracheal injection of 1 ml of a $TiO_2$ suspension in saline solution (20 mg/ml) and BCG, alone or in combination, did not show any retarded body weight increase in comparison with the untreated controls. No other information was available on the acute toxicity of titanium dioxide.(3)

### 2., 3., 4., 5., and 6. Subacute, Sensitization from Repeated Doses, Teratogenicity, Mutagenicity, and Carcinogenicity

The literature reviewed did not reveal any information or data on subacute toxicity, sensitization from repeated doses, teratogenicity, or carcinogenicity of titanium dioxide.

### 7. Other Chronic Studies

No evidence of any specific pathologic lesion produced by titanium dioxide was observed in rats following inhalation of the dust for 9-13 exposure

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1. L.P. Ereaux, "Clinical Observations on the Use of Titanium Salts in Man," Canadian Medical Association Journal, 73 (1955) p. 47

2. T.M. MacLeod and W. Frain-Bell, "The Study of the Efficacy of Some Agents Used for the Protection of the Skin From Exposure to Light," British Journal of Dermatology, 84 (1971) p. 266-81

3. C.J. Göthe and A. Swensson, op. cit., p. 579-85

months in the study by Christie et al, which was discussed in detail (pp. 64-5).(1) No information on other chronic toxicity studies in animals by any route was available.

### 8., 9., and 10. Behavioral Effects, Possible Synergisms, Other

No information.

### E. Toxicity - Lower Animals

No information.

### F. Toxicity - Plants

No information.

### G. Toxicity - Microorganisms

No information.

### H. Effects On Inanimate Objects and Structures

No information.

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1. H. Christie, R.J. MacKay and A.M. Fisher, op. cit.

# IV. REGULATIONS AND STANDARDS

## A. Current Regulations

### 1. Food and Drug Authorities

Regulations appear to make a differentiation between "color additives" and "food additives." The dyes or pigments, which are added to food, drugs or cosmetics, are generally "color additives" and those which are used in containers, films, coatings or other materials that are in contact with but not transferred to food are generally "food additives."

Amendments to the Federal Food, Drug and Cosmetic Act, Part 8-Color Additives, Subparts D and F, regarding titanium dioxide as a color additive state that $TiO_2$ be free from admixture with other substances. Specifications stipulate that $TiO_2$ conform to the following:(1)

Lead (as Pb), not more than 10 parts per million.
Arsenic (as As), not more than 1 part per million.
Antimony (as Sb), not more than 2 parts per million.
Mercury (as Hg), not more than 1 part per million.
Loss on ignition at 800°C. (after drying for 3 hours at 105°C), not more than 0.5 percent.
Water soluble substances, not more than 0.3 percent.
Acid soluble substances, not more than 0.5 percent.
$TiO_2$ not less than 99.0 percent after drying for 3 hours at 105°C.

Lead, arsenic, and antimony shall be determined in the solution obtained by boiling 10 grams of the titanium dioxide for 15 minutes in 50 milliliters of 0.5N hydrochloric acid.

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1. "Color Additives" -- Part 8, Title 21, Federal Register, loc. cit.

In coloring foods $TiO_2$ is restricted for use:(1)

(1) "The quantity of titanium dioxide does not exceed 1 percent by weight of the food.

(2) It may not be used to color foods for which standards of identity have been promulgated under section 401 of the act unless added color is authorized by such standards."

In packaging materials such as paper, adhesives, textiles, cellophane, resinous and polymeric coatings, which contain titanium dioxide, the use of $TiO_2$ is generally listed as authorized for use without any specified limitations. Occasionally the limitations simply state that use be consistent with good manufacturing practice.

## 2. and 3. Air, Water, and Ocean Dumping

In its Title 40 -- Protection of the Environment, Chapter 1, EPA has issued Ocean Dumping Criteria (Subchapter H, Part 227) in which titanium dioxide wastes are classified under Section 227.41, entitled "Materials Requiring Special Care," EPA stipulates that titanium dioxide wastes come under the category of materials for which permits may be issued for its dumping, if the applicant can demonstrate "(1) through the use of acceptable bio-assay or other scientific data that dumping of the material in the proposed quantities and qualities will have minimal adverse effects on the ocean environment" and "(2) that the material proposed for dumping contains less than the limiting permissible concentration of total pollutants" as stated in Section 227.71 entitled "Limiting Permissible Concentrations."(2)

## 4. Occupational Safety and Health Administration

Under the Occupational Safety and Health Standards, announced by OSHA in mid-1974, $TiO_2$ is listed in a table of air contaminants for which employee exposure limits are given as 8-hour time weighted averages. Thus OSHA has established that for any 8-hour work shift of a 40-hour week, an

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1. "Color Additives" -- Part 8, Title 21, Federal Register, loc. cit.
2. "Ocean Dumping Criteria," Federal Register, 38 (94), (16 May 1973) p. 12873

employee's exposure to $TiO_2$ shall not exceed the 8-hour time weighted average of 15 $mg/M^3$.(1)

### 5. Department of Transportation

Titanium dioxide does not appear on the DOT's List of Hazardous Materials. However, both titanium tetrachloride and titanium sulfate solution, containing not more than 45 per cent sulfuric acid, are listed.(2)

### 6. and 7. Other Federal and State Regulations

There were no additional regulations reported.

### 8. Foreign Countries

The Inter-Governmental Maritime Consultative Organization (IMCO) does not list $TiO_2$ in its International Maritime Dangerous Goods Code although titanium tetrachloride is listed.(3)

## B. Consensus and Similar Standards

### 1. and 2. Threshold limit Value (TLV) and Public Exposure Limits

The American Conference of Governmental Industrial Hygienists identifies $TiO_2$ as an "inert" or nuisance dust and, in accordance with their general rule for substances in this category, they recommended a TLV of 10 $mg/M^3$ for $TiO_2$.

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1. "Occupational Safety and Health Standards," Federal Register, 39 (125), (27 June 1974) p. 23542
2. Code of Federal Regulations 49 Transportation. (Washington, D.C.: GPO 1972) p. 39
3. International Maritime Dangerous Goods Code, IMCO. (London: Unwin Brothers Ltd., n.d.)

## 3. Other Regulations and Standards

### a. American Industrial Hygiene Association

As part of their Hygienic Guide Series, The American Industrial Hygiene Association reported on titanium dioxide summarizing: hygienic standards, including recommended maximal atmospheric concentrations [(8 hours): 15 $mg/m^3$] exposure tolerances, and atmospheric concentration immediately hazardous to life; toxic properties, including inhalation, skin contact, and ingestion; industrial hygiene practice, including industrial uses, evaluation of exposures, and hazards and their recommended control; and medical information. Their concluding statement was that because of the chemical and physiological inertness of $TiO_2$, it is unlikely that an emergency could arise which would require medical attention.(1)

### b. Joint Group of Experts on the Scientific Aspects of Marine Pollution (GESAMP)

GESAMP is a joint group made up of IMCO, FAO, UNESCO, WMO, IAEA, UN experts. In the list of marine pollutants and their relative harmfulness, which they have developed, $TiO_2$ wastes appear. The GESAMP evaluation of $TiO_2$ wastes indicates that they are of slight harm to living resources but no special control action is indicated. Furthermore, their evaluation shows $TiO_2$ wastes to be a negligible hazard to human health and a negligible hindrance to maritime activities.(2)

### c. National Safety Council

Titanium dioxide is not listed per se on The National Safety Council's list although the broader category titanium and its compounds does appear.(3)

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1. "Titanium Dioxide," American Industrial Hygiene Association Journal, 27 (2), (March-April 1966) pp. 206-7
2. Bernt I. Dybern, "Water Pollution -- A Problem with Global Dimensions," Ambio, 3 (3-4), p. 143 (1974)
3. Chemical Safety References, Data Sheet 486, Revision A (Chicago: National Safety Council, 1968) p. 14

### d. ASTM

Specifications for $TiO_2$ pigments are available inasmuch as manufacturers of special pigments carefully control the composition and properties of their products. Each pigment grade and its formulation is held within close limits.

The ASTM's directions for testing $TiO_2$ specifications include composition, residue on a sieve test, oil absorption valve, color and tinting resistance, matter volatile at 105°C, and matter soluble in water.(1)

The corresponding ASTM designations include D 476-66, Titanium Dioxide Pigments and D 1394-63, Chemical Analysis of White Titanium Dioxide Pigments. ASTM BS 239, White Pigments for Paints, also incorporates BS 1851.

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1. Kirk-Othmer Encyclopedia of Chemical Technology. *op. cit.*, p. 407

## V. EVALUATION AND COMMENTS

### A. SUMMARY

The United States, with an estimated production capacity of 939,000 tons/yr of titanium dioxide, now consumes approximately 800,000 tons annually. Although $TiO_2$ ranked only 48th in the production list of the 50 biggest-volume chemicals in 1972, it is industrially significant because of its unique contribution to the manufacture of so many commonly-used products, such as paint, paper and plastics.

Historically, titanium dioxide, *per se*, has been recognized as an innocuous compound, primarily due to its chemical inertness and its insolubility in water and most organic solvents. It is, however, classified as a nuisance dust and prolonged exposure to $TiO_2$ dust, or exposure to excessive amounts, has caused respiratory irritations. There is no indication, however, that the effects of $TiO_2$ in any way resemble those attributed to silica (silicosis), beryllium (berylliosis), or asbestos (asbestosis). In fact, it is utilized beneficially in preparations for the treatment of dermal irritations and has been used as a sunscreen.

Central to current environmental concern is the potential effect of and the disposition of the waste products from $TiO_2$ manufacture. By their very nature, the gaseous emissions and the acidic effluents involved are corrosive and capable of producing deleterious effects. Such characteristics highlight the significance of effective control with its attendant engineering problems and cost. In addition, environmental regulatory agencies are pressing for the development of controls that will decrease the potential environmental hazards.

### B. CONCLUSIONS

Until recently, manufacturers of $TiO_2$ faced no problems relative to the source of the necessary raw materials. Now, there is developing concern about the future availability of rutile ore to supply the increasing number of facilities utilizing this ore in the chloride process. Consequently, these manufacturers must find ways of increasing supplies of a high titanium dioxide-content raw material either by beneficiation of the lower-purity ilmenite or by the use of mixed feeds. Although existing technology indicates that this problem will be solved, the solution will bring with it a continuation, or a magnification, of some of the environmental problems that plague the industry at present, and may even introduce new problems.

The existing problems of $TiO_2$ processing waste disposal must be settled soon in a manner satisfactory to industry and government. Along with the development of new manufacturing technology, should go process innovations for the recovery and use of waste materials.

Landfill is the presently accepted disposal method for the solid wastes involved, but there is no record of research to determine the magnitude and potential long-term hazards of the leaching out of trace toxic metals from these wastes into the surrounding soil and waters. This issue, as well as the determination of the magnitude and potential problems of waste effluents from $TiO_2$ consuming industries, might become the subject for other future studies.

The lack of literature in a number of pertinent areas necessary to determine the total health and environmental effects of $TiO_2$, such as environmental transport, bioconcentration and biomagnification, and toxicity, hinders the completeness of analysis and evaluation, and suggests the need for further studies.

In conclusion unless new findings from current research, not published, or from future research contradict the prevailing views, it can be concluded that $TiO_2$, per se, does not pose substantial environmental hazard.

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## TECHNICAL REPORT DATA

*(Please read Instructions on the reverse before completing)*

1. REPORT NO.
EPA-560/2-75-001

2.

3. RECIPIENT'S ACCESSION NO.

4. TITLE AND SUBTITLE
Literature Study of Selected Potential Environmental
Contaminants
Titanium Dioxide

5. REPORT DATE
May 1975

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)

8. PERFORMING ORGANIZATION REPORT NO.
C-77354

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Arthur D. Little, Inc.
Acorn Park
Cambridge, Massachusetts 02140

10. PROGRAM ELEMENT NO.
2LA328

11. CONTRACT/GRANT NO.
68-01-2688

12. SPONSORING AGENCY NAME AND ADDRESS
Office of Toxic Substances
Environmental Protection Agency
Washington, D.C. 20460

13. TYPE OF REPORT AND PERIOD COVERED
Final

14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

16. ABSTRACT

A comprehensive review of the literature published since 1 January 1954 was conducted to prepare this preliminary report on the physical and chemical properties of titanium dioxide ($TiO_2$), on the environmental exposure factors related to its consumption and use, on the health and environmental effects resulting from exposure to $TiO_2$, and on the regulations and standards governing its use.

Titanium dioxide is industrially significant because of its unique contribution to the manufacture of such commonly-used products as paint, paper and plastics. Historically, $TiO_2$ has been recognized as an innocuous compound, but it is classified as a nuisance dust to which prolonged exposure can cause respiratory irritations. Current problems include concern about the future availability of rutile ore to supply the increasing number of facilities using this ore in the chloride manufacturing process, and the disposal of the high volume of $TiO_2$ manufacturing wastes, particularly the spent sulfuric acid and ferrous sulfate from the sulfate manufacturing process. On the basis of reported information, $TiO_2$ does not pose substantial environmental hazard.

17. KEY WORDS AND DOCUMENT ANALYSIS

| a. DESCRIPTORS | | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group |
|---|---|---|---|
| anatase | pollution | environmental exposure | 06/F,J,T |
| environmental contaminants | utilization | environmental effects | 07/B,D |
| pigments | | physical properties | |
| rutile | | chemical properties | |
| titania | | | |
| titanium dioxide | | | |
| production capacity | | | |

| | | |
|---|---|---|
| 18. DISTRIBUTION STATEMENT<br>Release unlimited | 19. SECURITY CLASS *(This Report)*<br>unclassified | 21. NO. OF PAGES<br>130 |
| | 20. SECURITY CLASS *(This page)*<br>unclassified | 22. PRICE |

EPA Form 2220-1 (9-73)